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FINAL REPORT (U)

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Prepared for the U.S. Department of Energy under Contract No. DE-AC09-89SR18035

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SANITARY LANDFILL
IN SITU BIOREMEDIATION OPTIMIZATION TEST
FINAL REPORT (U)

Authentication: _____

Terry C. Hazen

Prepared for the U.S. Department of Energy under Contract No. DE-AC09-89SR18035

Forward

This work was performed as part of a corrective action plan for the Savannah River Site Sanitary Landfill. This work was performed for the Westinghouse Savannah River Company Environmental Restoration Department as part of final implementation of a groundwater remediation system for the SRS Sanitary Landfill. Primary regulatory surveillance was provided by the South Carolina Department of Health and Environmental Control and the U. S. Environmental Protection Agency (Region IV). The characterization, monitoring and remediation systems in the program generally consisted of a combination of innovative and baseline methods to allow comparison and evaluation. The results of these studies will be used to provide input for the full-scale groundwater remediation system for the SRS Sanitary Landfill.

This report summarizes the performance of the Sanitary Landfill In Situ Optimization Test data, an evaluation of applicability, conclusions, recommendations, and related information for implementation of this remediation technology at the SRS Sanitary Landfill.

EXECUTIVE SUMMARY

The Savannah River Site (SRS) is a 320 square mile facility located in a rural area along the Savannah River, principally in the Aiken and Barnwell counties of South Carolina. The SRS is approximately 25 miles southeast of Augusta, Georgia, and 20 miles south of Aiken, South Carolina. The SRS is owned by the U.S. Department of Energy and operated by Westinghouse Savannah River Company. SRS has been in operation since 1950 with the mission to produce nuclear materials for national defense, medical, research, and space exploration. It has had 5 production nuclear reactors and 1 pilot scale reactor and all of the associated construction, fuel fabrication, processing, and waste handling operations associated with these activities during the last 40+ years. These operations and the people that worked at the site (as many as 50,000 during the early construction phases) generated large amounts of solid sanitary waste. During the first 20 years most of this waste was handled via burning rubble pits near major construction sites at SRS. In the early 1970's, these areas were consolidated into a single sanitary landfill located near the center of SRS, on Road C near Upper Three Runs Creek.

SRS Sanitary Landfill began receiving solid waste from site construction areas, offices, shops, and cafeterias in 1974 in its original 32 acre site. In 1987, as the original area reached its capacity, a 16-acre Northern Expansion and a 22-acre Southern Expansion were added. The Southern Expansion was filled and ceased operations in 1993. The Northern Expansion, also known as the Interim Sanitary Landfill (ISL) continued to receive SRS solid waste until October 1994. Though the ISL is still permitted to receive waste, it now only accepts special waste on a case by case basis and is rigorously controlled to ensure that hazardous waste is not accepted. During the course of its operation, the Sanitary Landfill received numerous materials that can leach or generate hazardous compounds, eg. paints, thinners, solvents, batteries, and rags and wipes used with F-listed solvents. The sanitary landfill was operated using the burrow and cover technique. Burrows were dug, waste was placed in the ditch and then covered with soil. Wastes were cataloged but not segregated within the landfill. In 1988, as a result of recurring evidence of hazardous constituents in the groundwater beneath the site, the Sanitary Landfill was designated as a Resource Conservation and Recovery Act (RCRA) Solid Waste Management Unit. In December 1989, the SRS was added to the National Priority List (NPL). At the time, the Sanitary Landfill was included in a combined RCRA/Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) unit list in the Federal Facilities Agreement (FFA). As a result of an ongoing RCRA permit investigation, the U.S. Environmental Protection Agency (EPA) removed the Sanitary Landfill from the combined RCRA/CERCLA unit list on August 29, 1991. The DOE and the South Carolina Department of Health and Environmental Control (SCDHEC) reached a settlement agreement (SW-91-51) in August 1991 outlining the steps that DOE would take to comply with the RCRA regulations. Principally, the DOE would close the portions of the landfill containing the solvent rags in compliance with Subpart G (Closure and Postclosure) of Part 265 (Interim Status Standards for Owners and Operators of Hazardous Waste Treatment Storage and Disposal Facilities) of the South Carolina Hazardous Waste Management Regulation (SCHWMR). The settlement agreement also states that the DOE shall submit a RCRA Postclosure Part B Permit Application on March 31, 1993 (WSRC 1993a), for the portions of the landfill that received the solvent rags. The RCRA Postclosure Part B Permit Application, submitted on March 31, 1993, contained an Alternate Concentration Limit (ACL) Demonstration. On March 31, 1994 a Corrective Action Plan (CAP) based on the assumption that the ACL Demonstration would be approved was submitted to SCDHEC which addressed corrective actions to remediate the groundwater at the Sanitary Landfill. Based on an evaluation of groundwater analytical data for the period of 1984 through 1993 (up to and including 2Q93), as described in the

CAP, the GWPS has been exceeded at or downgradient of the Point of Compliance (POC) for vinyl chloride (VC) and trichloroethylene (TCE).

As part of the CAP, Westinghouse Savannah River Company Environmental Restoration Department (WSRC-ER) subcontracted Camp Dresser and McKee Federal to do an Interim Technology Screening Report for evaluating remediation of contaminated groundwater and vadose zone using EPA guidance (EPA/540/G-89/004). The vadose zone evaluation report determined that "No action" was necessary. The groundwater report evaluated more than 100 process options for groundwater remediation. The initial screening for ease of implementation reduced the options to 40. The second screening evaluating each technology for: 1) overall protection of human health and the environment, 2) compliance with applicable or relevant and appropriate requirements, 3) long-term effectiveness, 4) reduction of toxicity, mobility, or volume, 5) short-term effectiveness, 6) ease of implementation, and 7) cost. Eight alternatives made it through the second screening. Of these eight, aerobic in situ bioremediation was ranked the highest and deemed the most appropriate for the SRS Sanitary Landfill. Previous studies and on-going demonstrations at SRS had shown that normal soil bacteria are capable of degrading chlorinated solvents in situ if they are stimulated with oxygen and additional nutrients. In situ biodegradation is a highly attractive technology for remediation because contaminants are destroyed in place, not simply moved to another location or immobilized, thus decreasing costs, risks, and time, while increasing efficiency and public and regulatory acceptability. Bioremediation has been found to be among the least costly technologies in applications where it is feasible. Full scale demonstrations of this technology have already been completed as part of the SRS Integrated Demonstration at a solvent disposal basin system in M-area (Hazen, 1994). Because the M basin differed from the Sanitary Landfill in having only TCE and tetrachloroethylene (PCE), no other waste disposal, and a groundwater that was only aerobic (> 2 mg/L dissolved oxygen), it was decided that a treatability study was prudent for the Sanitary Landfill. The nine week bench-scale treatability test was done to determine: 1) if the contaminants of concern (COC), (VC, TCE, and chlorobenzene) were biodegradable in the specific soil and groundwater samples. This included determining if pretreatment was necessary to dilute inhibitory compounds, 2) the rates of biodegradation of the COCs, 3) the extent of contaminant biodegradation, and 4) the optimal conditions for biodegradation, including nutrient optimization and choice of inoculum.

The treatability study using soil columns to simulate both vadose and groundwater conditions used soil and groundwater from the most contaminated area of the Sanitary Landfill. These studies showed that all of the COCs were biodegradable by indigenous soil bacteria and that their ability to degrade the COCs to undetectable levels greatly exceeded the highest concentrations found at the Sanitary Landfill. The soil column simulations showed that the biostimulated soil microbes could reduce more than 100,000 ppb of the contaminants in water to undetectable levels in just a few days (the highest concentrations observed at the Landfill has been 100 ppb). The treatability study showed that the COCs were biodegraded in both the saturated and unsaturated soil columns. The major limitation to soil microbes at the SRS Sanitary Landfill was oxygen, supplemental carbon sources (methane), and trace nutrients (phosphorus and nitrogen), in that order.

Historical groundwater data and landfill usage information confirmed that there existed two separate plumes of concern. One plume contained TCE as its major contaminant of concern and the other plume contained VC as its major constituent. Because these two plumes were also quite different in terms of dissolved oxygen concentration, total organic, and other trace nutrients a pilot-scale optimization test was deemed necessary to determine the best strategy for both plumes and

also to gather critical physical and chemical information as input for the final remediation system for the two parts of the landfill. This pilot-scale optimization test is the focus of this report.

The optimization test objectives were to determine the optimum design parameters for full-scale operation including: 1) radial air/methane flow patterns in the saturated and vadose zones, 2) attainable radius of influence (ROI) for the various injection pressures and vacuum pressures in the saturated and vadose zones, 3) the need for hydraulic controls to prevent outward spreading of contaminants from the sparge wells, 4) air injection/extraction flow rates associated various injection/extraction pressures, 5) air/methane injection rates that optimize biodegradation of chlorinated solvents in both the saturated and vadose zones, 6) biodegradation rates for trichloroethylene, vinyl chloride, chlorobenzene, and methane in the vadose and saturated zones under various test conditions, 7) identification of densities of methanotrophs and chlorobenzene degraders present at sites 1 and 2, 8) the rate of trichloroethylene, vinyl chloride, chlorobenzene, and methane loss under test conditions, and 9) the feasibility of using vertical air injection wells (AIW) for full-scale treatment. Two sites were field tested adjacent to the Sanitary Landfill Southern Expansion. Each site was set up with 18 sampling and injection wells. Three air injection wells were positioned to provide overlapping 20 ft radii and a vacuum was applied to a central air sampling well to provide a controlled air sampling ROI. Air, nutrients (nitrous oxide and triethyl phosphate), and methane were introduced sequentially to determine the ability of each nutrient to stimulate bioremediation.

The test system's subsurface component installation, (i.e. injection screen zone and saturated zone piezometer locations) and the local soil structure exhibited a highly sensitive relationship for a pressure vs. flow threshold as defined for the subsurface soil composition of the Sanitary Landfill (DCN; 5112-005-RP-BFBC). The estimated hydraulic conductivity in the saturated zone at site 1 was $2.30\text{E-}04$ m/s, while site 2 was $9.97\text{E-}05$ m/s. These estimated hydraulic conductivity values correlate well with the values presented by Freeze and Cherry (1989). In addition, the estimated hydraulic conductivity values also correlate well with the values obtained for the 1994 field permeability testing of the "D" level wells at the Sanitary Landfill. The lowest recommended hydraulic conductivity for biostimulation using liquid nutrient injection is $10\text{E-}6$ m/s and for gaseous nutrient injection or extraction $10\text{E-}11$ m/s (Baker and Herson, 1990).

Pressures below the screen zone head pressure threshold were not great enough to force air into the groundwater, but once the threshold was exceeded, (> 10.5 psig at site 1 and > 6 psig at site 2) the pressure/flow characters immediately exhibited biosparging characteristics, as evidenced by air flow out of associated saturated zone piezometers and pressure differentials in the unsaturated zone piezometers. In addition, due to the ease of air injection from limited head pressures and fluid sand conditions in the screen zones the biosparging regime operated in a narrow pressure/flow range, (± 1 psig). Increases above that range created preferential flow paths between the injection wells and associated saturated zone sampling points (i.e. piezometers) thereby short circuiting biosparging. This phenomena for the proposed full-scale remediation system is very unlikely to occur due to its increased depths, lengths and distances to existing monitoring wells and newly designed sampling and monitoring points associated with the proposed system.

Site 1 and Site 2 were also significantly different in terms of COCs, dissolved oxygen, chloride, nitrite, and nitrate concentrations, and response to nutrient stimulation, thus each site is considered separately. Overall, both sites were found to have indigenous microorganisms that could be stimulated to degrade chlorobenzenes, trichloroethylene and, its daughter product, vinyl chloride in situ by the addition of oxygen (as compressed air), nutrients, and methane to the contaminated

zone. Biostimulation at both sites resulted in undetectable levels of COCs and many other organics in both the groundwater and vadose zone. It was also shown that chloride concentrations in the groundwater at both sites increased significantly as bacteria densities increased. This correlation shows that biodegradation of chlorinated solvents in situ was complete and resulted in production of chloride.

Site 1 had lower levels of carbon, lower levels of natural biological activity, higher oxygen levels, and TCE as the COC. This coincides well with the newer refuse source components in this part of the landfill. The groundwater dissolved oxygen (DO) was at or below 20% saturation normally; however, it could be raised to >95% saturation after only 5 h of air injection. Once the air injection was shut off, the DO saturation returned to < 20% in 4 h. TCE concentration did not change when air alone was the stimulus. When gaseous nutrients were added to the air some decrease in TCE concentration was observed; however, when methane was also added to the nutrient air mixture, the TCE concentration in all affected wells declined to non detect levels (<2 ppb). After the air/nutrient/methane injection was ceased the TCE was detectable in 7 days and reached low pre-injection levels within 3-4 weeks. Biodegrader densities increased only slightly during air alone injection, but increased 2-3 orders of magnitude after air/nutrient/methane injection was started. The densities of biodegraders slowly declined over the course of the campaign. After several weeks the densities of biodegraders still had not reached pre-injection levels. Statistical analyses showed that there was a significant positive correlation between DO and biodegrader density, i.e. as the DO increased, the number of bacteria increased. Nitrate was low in shallow wells and high in deeper wells. Conversely nitrite was higher in shallow wells and low in deep wells. In addition, nitrite could not be detected while air was being injected. Since nitrate is required nutrient for biological activity and nitrite is a daughter product of denitrification under anaerobic conditions, this suggests that the shallow wells have higher amounts of total biological activity and that air injection can create bulk aerobic conditions at this site. All of the data from this site demonstrate that oxygen is limiting to the biodegraders at this site, but that air injection alone is insufficient to affect bioremediation of the site. Carbon, nitrogen and phosphate must be supplied to bioremediate the site to non detect concentrations. Biodegrader activity at this site can be maintained at a level effective for groundwater bioremediation by pulsed injection of gaseous nutrients and a carbon source. Monthly groundwater monitoring should be sufficient to maintain an appropriate pulse schedule.

Site 2, as compared to site 1, had lower DO (<15% saturation), higher chloride, nitrite, and total carbon concentrations, and VC and chlorobenzenes as COCs. This again reflects the nature of the point source as being refuse that was put in the landfill many years earlier than site 1. This has allowed more leaching and thus more biological activity which created the VC from TCE under anaerobic conditions caused by the higher carbon content. This higher biological oxygen demand was well demonstrated at site 2 by the respiration experiment which showed that air injection could only increase the DO saturation from 15 to 30%. After the air injection was stopped the DO saturation slowly returned to pre-injection levels after 24 h. All of the chlorinated solvents declined significantly with air alone injection reaching non detect very quickly. The chlorobenzenes declined after nitrous oxide and triethyl-phosphate were also added to the gas injection. After air injection stopped COCs increased very slowly not reaching pre-injection concentrations for several weeks. Contaminant-degrader densities increased 2-3 orders of magnitude after air injection was started and declined slowly after air injection was stopped. Nitrite was undetectable when air was on and > 10 ppm when air was off. Chloride concentrations were always higher when air was being injected and increased concomitantly with increases in contaminant degraders and decreases in chlorinated solvents. These studies show that air injection at this site can stimulate contaminant

degraders to completely mineralize contaminants to non-detect levels. They also show that enough co-metabolic carbon is present in this environment that methane injection is not necessary. Air injection increases the DO concentration enough to stop anaerobic process as evidenced by the non-detection of nitrite, but not enough to saturate the environment. Monthly monitoring and pulsed injection of air with occasional nitrogen & phosphorous gaseous supplements should be all that is necessary to maintain complete bioremediation of solvents at this site.

The final remediation system should incorporate 2 injection zones along the south and west sides of the landfill, respectively. Since groundwater consistently flows parallel to the long axis of the SRS landfill two horizontal wells, one running along the south side of the southern expansion and the other along the west side should be able to bioremediate any solvents coming from the site. Based on the optimization test and probable future leaching changes both injection systems should inject at a depth of 20-30 ft below the water table. This will provide a sparge zone that will biotreat all current and future leachate since the proposed configuration and prevailing groundwater flow would contain any leachate from these areas. Cost analysis will determine if horizontal wells or a series of vertical injection wells are most appropriate. The injection system will consist of a compressor with the ability to add nitrous oxide, triethyl-phosphate, and methane. The south side injection will need to be controlled separately from the west side injection, since different strategies will be necessary for the most cost effective in situ bioremediation. Both wells will, however, need all capabilities since conditions may change as the landfill ages. The results of the Bioremediation Optimization Test have shown that the use of bioremediation via in situ stimulation of indigenous microorganisms is an efficient and cost effective long-term means of obtaining ultimate groundwater restoration at the SRS Sanitary Landfill.

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1.0 Introduction

The Savannah River Site (SRS) is owned by the U.S. Department of Energy (DOE) and operated by Westinghouse Savannah River Company, with the mission to produce nuclear materials for national defense medical research & space exploration. The SRS is an approximately 320 square mile facility located in a rural area along the Savannah River, principally in the Aiken and Barnwell counties of South Carolina.

In 1974, the SRS Sanitary Landfill began operations and received solid waste from site construction areas, offices, shops, and cafeterias. During the course of its operation, the landfill received rags and wipes used with F-listed solvents (WSRC, 1993a). In 1988, as a result of recurring evidence of hazardous constituents in the groundwater beneath the site, the Sanitary Landfill was designated as a Resource Conservation and Recovery Act (RCRA) Solid Waste Management Unit. During 1994, a RCRA Corrective Action Plan (CAP), based on the assumption the Alternate Concentration Limit (ACL) would be approved, was submitted to the South Carolina Department of Health and Environmental Control (SCDHEC). The CAP defined the actions necessary to reduce contaminant (trichloroethylene and vinyl chloride) concentrations below Groundwater Protection Standards (GWPS). The selected remedial technology, for the SRS Sanitary Landfill was in-situ bioremediation.

The Sanitary Landfill Bioremediation Optimization Test was conducted to support the development input data necessary to provide the design of the future in situ groundwater bioremediation system for the landfill as mandated by the CAP. This report provides the technical and scientific data analysis and interpretation from the optimization test results. Upon design completion and approval from the regulators, the in situ bioremediation system will be installed allowing the corrective action to be initiated at the SRS Sanitary Landfill. The system will provide the means necessary to reduce volatile organic compound (VOC) groundwater contaminant concentrations to levels at or below compliance criteria of the Groundwater Protection Standards.

1.1 Site Description

The SRS Sanitary Landfill is an approximately 70-acre site and is located between B Area and Upper Three Runs Creek. It was originally opened in 1974 as a 32-acre site. In 1987, as the original area reached its capacity, a 16-acre Northern Expansion and a 22-acre Southern Expansion were added. The Southern Expansion ceased operations in 1993. The Northern Expansion, also known as the Interim Sanitary Landfill although open, is not receiving waste on a regular basis. The Northern Expansion is currently under rigorous administrative control to ensure that hazardous waste is not accepted. Currently, all sanitary wastes from SRS are removed to a controlled landfill off-site by a subcontractor.

1.1.1 Site Characteristics

Elevation of the Sanitary Landfill ranges from approximately 240 feet above msl at the northwestern corner to about 170 feet above msl at the southeast corner. South of the landfill is a wetland, which makes up the flood plain for Upper Three Runs Creek in this vicinity. It is believed that this flood plain and creek constitute the discharge region for groundwater (in the Steed Pond Aquifer) downgradient from the Sanitary Landfill.

The Steed Pond Aquifer (Water Table Aquifer) is the shallowest hydrostratigraphic unit underlying the Sanitary Landfill. The aquifer consists of the saturated unit extending from the water table down to the top of the principle confining unit (Meyers Branch Confining System). The thickness of the Steed Pond Aquifer ranges from 180 feet in the northern portion of the landfill to 110 feet in the southern portion of the landfill.

The Steed Pond Aquifer, in the vicinity of the landfill, lacks competent confining units above the Meyers Branch Confining System; therefore, an informal system was developed to define the screen zones within the Steed Pond Aquifer. These screen zones are defined as:

- Screen Zone B: Screen set just above the Meyers Branch Confining System
- Screen Zone C: Screen set approximately 25-30 feet below water table surface
- Screen Zone D: Screen set to intercept the water table surface.

Recent characterization activities are discussed in the report entitled, "Summary Report for the Subsurface Characterization at the Sanitary Landfill (U), WSRC-TR-94-0263", dated May 1994. This report suggests that the groundwater flows in a southerly gradient (Fig 1.1).

1.1.2 Regulatory history

During the course of its operation, the Sanitary Landfill received rags and wipes used with F-listed solvents. In 1988, the Sanitary Landfill became the subject of RCRA Facility Investigation and was designated as a RCRA Solid Waste Management Unit (SWMU) due to recurring evidence of RCRA/hazardous constituents in the groundwater beneath the site. In December 1989, the SRS was added to the National Priority List (NPL). At the time, the Sanitary Landfill was included in a combined RCRA Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) unit list in the Federal Facilities Agreement (FFA). As a result of an ongoing RCRA permit investigation, the U.S. Environmental Protection Agency (EPA) removed the Sanitary Landfill from the combined RCRA/CERCLA unit list on August 29, 1991.

The DOE and the SCDHEC reached a settlement agreement (SW-91-51) in August 1991 outlining the steps that the DOE would take to comply with the RCRA regulations. Principally, the DOE would close the portions of the landfill containing the solvent rags in compliance with Subpart G (Closure and Postclosure) of Part 265 (Interim Status Standards for Owners and Operators of Hazardous Waste Treatment Storage and Disposal Facilities) of the South Carolina Hazardous Waste Management Regulation (SCHWMR).

The settlement agreement also states that the DOE shall submit a RCRA Postclosure Part B Permit Application on March 31, 1993 (WSRC 1993a), for the portions of the landfill that received the solvent rags. The RCRA Postclosure Part B Permit Application, submitted on March 31, 1993, contained an ACL Demonstration. On March 31, 1994 a CAP, based on the assumption the ACL demonstration would be approved, was submitted to SCDHEC which addressed corrective actions to remediate the groundwater at the Sanitary Landfill. Based on an evaluation of groundwater analytical data for the period of 1984 through 1993 (up to and including 2Q93), as described in the CAP, the GWPS has been exceeded at or downgradient of the Point of Compliance (POC) for vinyl chloride and trichloroethylene.

1.2 Waste Stream Description

The Sanitary Landfill received all site generated sanitary solid wastes from a variety of sources, including site construction areas, offices, shops, and the cafeteria from 1974 until 1993. During the course of its operation, the Sanitary Landfill received numerous materials that can leach or generate hazardous compounds, e.g. paints, thinners, solvents, batteries, and rags and wipes used with F-listed solvents (i.e. RCRA listed waste).

1.2.1 Waste Matrices

The sanitary landfill was operated using the burrow (open trench) and cover technique. Burrows were dug, waste was placed in the open trench and then covered with soil. Wastes were cataloged but not segregated within the landfill.

1.2.2 Waste pollutants/contaminants

New wells were installed as part of recent characterization studies at the Sanitary Landfill and were first sampled between March and April 1994. Analytical data for 2Q94 are plotted for vinyl chloride, Screen Zone D (Fig. 1.2), trichloroethylene, Screen Zone D (Fig. 1.3), tetrachloroethylene, (PCE), Screen Zone D (Fig. 1.4), and chlorobenzene, Screen Zone D (Fig. 1.5). These contaminant maps were utilized in the selection of Bioremediation Optimization Test locations.

The plume data reveals that two distinctive contaminant plumes exist at the landfill. The contaminant in the southern portion or south of the landfill is predominantly TCE while the contaminant is predominantly vinyl chloride. Sites 1 and 2 were located in these plumes to verify the adequacy of the remediation technology selection.

Site 1 is located south of the southern expansion section of the landfill. This area of the landfill received refuse more recently than the main portion of the landfill. Also it is known from landfill records that much of the refuse was construction debris and rubble. Thus available carbon sources are lacking. Given these conditions full scale remediation should only occur after a carbon source (i.e. methane) is introduced to the site.

Site 2 is located southwest of the original landfill plot and west of the southern expansion. This area of the landfill received more organic material but since the microorganisms have been present for some time available oxygen is lacking. Given these facts it is felt that the major microorganism activity is anaerobic. This is supported by the fact that the major contaminant at this site is vinyl chloride which is a daughter product of anaerobic degradation of PCE.

1.3 Treatment Technology Evaluation and Selection

The corrective action for the Sanitary Landfill, as described in the CAP, consists of in-situ bioremediation and will be implemented in a phased approach. After each phase, the effectiveness of treatment will be evaluated and the need for subsequent phase(s) assessed. Phase 1 will consist of installing a impermeable clay cap and an in-situ bioremediation system at the downgradient edge of the landfill; a second bioremediation system will be installed, if required.

The selected technology for remediating groundwater at the Sanitary Landfill is an in-situ bioremediation system with air injection into the saturated zone. Horizontal or vertical well(s) will be installed near the bottom of the contaminant plume. Air will be injected into the saturated zone to induce two processes. The first process is the oxygenation of the saturated zone which will stimulate aerobic microbial growth and contaminant degradation. The second process involves oxygenation of the unsaturated zone. Any volatilization of VOCs that occurs in the saturated zone will induce the air/vapor bubbles to migrate upward into the unsaturated zone. The bubbles will cause the unsaturated zone to become oxygen rich and thus enable the unsaturated zone to support aerobic bioremediation as well. The microbes present will degrade the organic compounds to carbon dioxide, water, and hydrochloric acid. This process was successfully demonstrated at the Integrated Demonstration Site in the A/M Area of the SRS. Methane (at concentrations of up to 4 % by volume) was injected beneath the contaminated plume where it was used as a carbon and energy source by methanotrophic microorganisms. These microorganisms produce an enzyme called methane monooxygenase which is an extremely powerful oxidizer that can oxidize chlorinated solvents. The SRS demonstration has shown that this enzyme is effective in oxidizing trichloroethylene without producing toxic products of incomplete oxidation, such as vinyl chloride.

The bioremediation system will operate without a vapor extraction and offgas treatment system. By carefully monitoring the amount of air injected, the cognizant engineer can ensure that sufficient oxygen is available for volatilization and bioremediation. Excess air injection will be avoided as this could create rapid diffusion of the VOCs to the surface before the microorganisms have had sufficient time to degrade them. This would result in the evolution of VOCs as fugitive emissions from the soil surface. This system will operate entirely in-situ and will not produce waste products that must be treated or disposed. Air and water discharge permits will not be required for the operation of this system. This system was selected for its low cost, simple operation, lack of waste generation, its ability to remediate the organic contaminants to the required GWPSs, and its flexibility for phasing in additional technologies (e.g., vapor extraction, sparging, etc.) if needed.

Subsequent corrective action measures may be instituted based on the results of the first phase; these may include vadose zone bioremediation, air stripping of groundwater and the vadose zone, source control, and treating the off gases resulting from sparging activities.

Based on the assumption that the 1992 RCRA Part B Permit Renewal Application (U), Savannah River Site, Volume XXIII, Books 1-4, Sanitary Landfill Postclosure is acceptable to regulators, which includes the ACL Demonstration and CAP, additional activities will be required to fully design and execute corrective measures.

1.3.1 Treatability Study

Bench-scale treatability testing was performed, during 1993, using Sanitary Landfill soil and groundwater samples. Historical groundwater data and landfill usage information confirmed that there existed two separate plumes of concern. One plume contained TCE as its major contaminant of concern and the other plume contained vinyl chloride as its major constituent. The treatability testing confirmed the potential of using existing indigenous microorganisms to degrade the existing groundwater contaminants. During the testing several chemical and microbiological parameters were evaluated. The nine week test was done to determine: 1) if the contaminants of concern (COC), (VC, TCE and chlorobenzene) were biodegradable in the specific soil and groundwater samples. This included determining if pretreatment was necessary to dilute inhibitory compounds, 2) the rates of biodegradation of the COCs, 3) the extent of contaminant

biodegradation, and 4) the optimal conditions for biodegradation, including nutrient optimization and choice of inoculum.

Soil columns used to simulate both vadose and groundwater conditions contained soil and groundwater from the most contaminated areas of the Sanitary Landfill. This showed that all of the COCs were biodegradable by indigenous soil bacteria and that their ability to degrade the COCs to undetectable levels greatly exceeded the highest concentrations found at the Sanitary Landfill. The soil column simulations showed that the biostimulated soil microbes could reduce more than 100,000 ppb of the contaminants in water to undetectable levels in just a few days (the highest concentrations observed at the landfill has been 100 ppb). The treatability study showed that the COCs were biodegraded in both the saturated and unsaturated soil columns. The major limitation to soil microbes at the SRS Sanitary Landfill was oxygen; however, additional carbon sources (methane) and trace nutrients (phosphorus and nitrogen) greatly increased the rate of biodegradation. The bench-scale test concluded that biodegradation in the field was possible, but may be limited by oxygen, nutrients and available carbon sources. A detailed account of the bench-scale treatability test can be found in treatability study test report.

1.3.2 Optimization Test Plan

Because the two plumes were also quite different in terms of dissolved oxygen concentration, total organics, and other trace nutrients a pilot-scale optimization test was deemed necessary to determine the best strategy for both plumes and also to gather critical physical and chemical information for the two parts of the landfill to determine the best functional future criteria for the full scale remediation system. Camp Dresser & McGee Federal was again tasked to prepare the Sanitary Landfill In Situ Bioremediation Optimization Test Plan. The Optimization Test Plan is a detailed document that provides the strategy, dynamics and technical information necessary to design, engineer and implement the installation of key components including all major injection and extraction systems, data acquisition controls and subsurface components for geophysical monitoring that were necessary to conduct the Optimization Test.

Figure 1.1 Hydraulic Gradient Map Third Quarter 1994.

3Q94

Figure 1.2 Vinyl Chloride Map Screen Zone D Second Quarter 1994.

Figure 1.3 Trichloroethylene Map Screen Zone D Second Quarter 1994.

Figure 1.4 Tetrachloroethylene Map Screen Zone D Second Quarter 1994.

Figure 1.5 Chlorobenzene Map Screen Zone D Second Quarter 1994.

2.0 Sanitary Landfill Optimization Test

The project was designed to assess the feasibility of and to develop optimization parameters for the design of the in-situ bioremediation system for treatment of groundwater contaminated with chlorinated solvents from the SRS Sanitary Landfill. Indigenous microorganisms were stimulated to degrade trichloroethylene and its daughter product vinyl chloride in-situ by addition of oxygen (as compressed air), organic nutrients, and methane to the contaminated zone. In-situ biodegradation is a highly attractive technology for remediation because contaminants are destroyed in place, not simply moved to another location or immobilized, thus decreasing costs, risks, and time, while increasing efficiency and public and regulatory acceptability. Bioremediation has been found to be among the least costly technologies in applications where it is feasible. The SRS Integrated Demonstration using horizontal wells provided significant evidence for feasibility of the technology as well as demonstrating advantages over conventional bioremediation nutrient delivery techniques. This project expanded on the data developed during the Integrated Demonstration and further incorporated the principles of biosparging and bioventing for treatment of contaminated groundwater. Biosparging is the addition of air into the groundwater in order to supply oxygen for bioremediation while volatilizing some contaminants into the vadose zone. Bioventing is the slow addition of oxygen to the vadose zone at a rate to meet the aerobic biodegradation needs of the indigenous organisms to biodegrade the contaminants being volatilized by the sparging wells.

Biodegradation was field tested and optimized for full-scale treatment. Methane induced biodegradation of trichloroethylene was tested at Site 1. Air/methane mixtures were demonstrated to stimulate selected members (methanotrophs) of the indigenous microbial community that degrade trichloroethylene. The second site (Site 2) tested the biodegradation of chlorobenzene as an inducer for the biodegradation of vinyl chloride. Bench-scale treatability data have demonstrated the potential for chlorinated solvents to be transformed by indigenous organisms which oxidize chlorobenzene at the Sanitary Landfill.

Air, nutrients (nitrous oxide and triethyl phosphate), and methane were introduced to stimulate bioactivity. Air, then air and nutrients were added before methane to determine if the existing field conditions and microbial populations were capable of degrading the chlorinated solvents but are oxygen and/or nutrient limited. Data from the previous demonstration of in situ bioremediation, where air/methane was injected, was used to provide base line chemical and biological responses and degradation rates.

Vertical Air Injection Wells (AIWs) provided the delivery of gases into the contaminated groundwater. A low flow vacuum was applied to the central Air Sampling Wells (ASWs) within the vadose zone to encourage air/nutrient/methane movement through the upper saturated zone and vadose zone and to control air flow within a designed radius of influence (ROI). Controlling the vapors within the ROI allowed for a more accurate determination of the system mass balance and utilization/biodegradation rates. In addition, off-gas from the ASWs and vadose zone piezometers was assayed for methane, trichloroethylene, tetrachloroethylene and chlorobenzene and potential break down products of trichloroethylene and tetrachloroethylene (e.g., dichloroethylene, vinyl chloride and carbon dioxide). Based on conservative estimates, the total emissions from site 1 and site 2 were calculated to be $2.31\text{E-}03$ lb/h and $1.02\text{E-}02$ lb/h, respectively. Based on these estimates, no off-gas treatment was required by the state.

2.1 Test Objectives and Rationale

The Bioremediation Optimization Test provides information on the field applicability of bioremediation and quantitative performance data for input into the design of a biosparging system that is capable of treating the groundwater downgradient of the Sanitary Landfill. The optimization test objectives were to determine the optimum design parameters for full-scale operation including: 1) radial air/methane flow patterns in the saturated and vadose zones, 2) attainable radius of influence (ROI) for the various injection pressures and vacuum pressures in the saturated and vadose zones, 3) the need for hydraulic controls to prevent outward spreading of contaminants from the sparge wells, 4) air injection/extraction flow rates associated with various injection/extraction pressures, 5) air/methane injection rates that optimize biodegradation of chlorinated solvents in both the saturated and vadose zones, 6) biodegradation rates for trichloroethylene, vinyl chloride, chlorobenzene, and methane in the vadose and saturated zones under various test conditions, 7) identification of densities of methanotrophs and chlorobenzene degraders present at sites 1 and 2, 8) the rate of trichloroethylene, vinyl chloride, chlorobenzene, and methane loss under test conditions, and 9) the feasibility of using vertical AIWs for full-scale treatment.

2.2 Experimental Design and Test Campaigns

Pilot test sites (Fig. 2.1) were selected based on the following requirements: 1) the sites were representative of the hydrogeology and contaminant concentrations for the proposed location of the full scale containment/treatment system; 2) sites were accessible for system installation and pilot operation; 3) existing monitoring wells were located beyond the sparging radius of influence of the pilot system to avoid short circuiting air flow in the saturated zone; and 4) sites avoided new stormwater detention basins associated with closure activities.

Two sites were field tested adjacent to the Sanitary Landfill Southern Expansion. Each site was set up with 18 sampling and injection wells. Three air injection wells were positioned to provide overlapping 20 ft radii and a vacuum was applied to a central air sampling well to provide a controlled air sampling ROI. Air, nutrients (nitrous oxide and triethyl phosphate), and methane were introduced sequentially to determine the ability of each nutrient to stimulate bioremediation.

Site 1 is shown in plan view on Fig. 2.2. The system at Site 1 is located approximately 150 feet south of the landfills southern boundary between existing monitoring wells LFW-38, LFW-59 and LDW-62. Trichloroethylene concentrations in groundwater collected from shallow wells (D wells) in the vicinity of the pilot system range from 8.3 to 46 micrograms per liter ($\mu\text{g/l}$) (8.3 to 46 ppb); deep wells (C Wells) range from 9 to 19 $\mu\text{g/l}$ (9 to 19 ppb). Vinyl chloride and chlorobenzene in the groundwater were below detection in these wells.

The stormwater retention basin at this site is located in the middle of the originally targeted area for the pilot test. Because of the basin installation, this pilot test location was moved from its original site, between wells LFW-59 and LFW-61 to its current site between wells LFW-38, LFW-59 and LFW-62. This location is less than ideal given the close proximity of existing monitoring wells and the stormwater basin. Water collection in the basin causes mounding of the water table after storms, groundwater movement, and, potentially, dilution effects in the pilot test area.

Site 2 is shown in plan view on Fig. 2.3. The pilot system at Site 2 is located approximately 80 feet west of the western boundary of the landfill Southern Expansion between existing wells

LFW-8 and LFW-48. Vinyl chloride concentrations at LFW-8 and LFW-48 (D wells) ranged from 94 to 143 and 85 to 129 $\mu\text{g/l}$, respectively. Vinyl chloride was not detected in deep wells (C wells) at these locations. Chlorobenzene concentrations in the groundwater at wells LFW-8 and LFW-48 ranged from 41 to 54 and 25 to 43 $\mu\text{g/l}$, respectively. Trichloroethylene was not detected in the groundwater in this area. Unlike Site 1, the stormwater basin and ditch did not influence groundwater recharge in the pilot test area, therefore, groundwater level monitoring within the basin and surrounding monitoring wells was not required.

The pilot system consists of three Air Injection Wells (AIWs) arranged in a triangular pattern with one central Air Sampling Well (ASW) located equidistant from each Air Injection Well, as shown in Figure 2.3. The ASW was operated under a vacuum, similar to a vapor extraction well. Flow rates and vacuum were reduced compared to a full vapor extraction system in order to minimize the mass of contaminants that are volatilized and extracted by the vacuum-blower. Instead, the air extraction system was operated at a level that contained vadose zone gases generated during air injection to prevent movement of vadose zone vapors away from the biosparging area. The purpose of the well configuration system is to:

- Retain vadose zone gases (i.e. contaminants, oxygen, nutrients, etc.), generated during biosparging, in one area to create a zone of optimal biodegradation
- Allow for a more accurate determination of the mass of contaminants and nutrients that move from the saturated to the vadose zone during biosparging
- Supplement oxygen levels in the vadose zone over those generated from air injection in the saturated zone.

To assure the ASW was not operated under flows and vacuums that caused extraction of vadose zone contaminants, the ROI for the ASW was adjusted to 20 feet, less than the full ROI of the AIWs.

Similar to the ASW, air injection for biosparging occurred at flow rates that provided a less than optimal ROI in order to minimize the rate of contaminant volatilization and increase the time for biodegradation to occur in the saturated zone. Air injection was adjusted to balance biodegradation of nutrients and contaminants in the saturated zone and the vadose zone.

The primary scenarios anticipated to occur at the site were:

- All nutrient and contaminant biodegradation occurs in the saturated zone with minimal or no release to the vadose zone.

Two other possible scenarios were:

- Biodegradation occurs in both the saturated and vadose zones with adequate nutrient supplies to stimulate methanotrophs and chlorobenzene degraders in both zones
- Nutrient utilization but no contaminant degradation occurs in the saturated zone and a large mass of contaminant is released to the vadose zone without a nutrient source.

Bench-scale tests indicated that all biodegradation should occur in the saturated zone. In addition, due to low concentrations of contaminants in the groundwater, it was anticipated that little or no vapors would be introduced into the vadose zone during biosparging.

One air compressor was used for air injection at both pilot test sites. The compressor station was located at the southwest corner of the Southern Expansion. Separate piping connected the station to the injection wells at each test site (see Fig. 2.4). Valves, flow meters, sampling ports, and pressure monitoring points are located such that each test plot can be monitored independently. In addition, valves (located on both sides of the branch points) and at each well head permitted individual adjustment of flow and pressure to each injection well.

A cross-sectional schematic of the pilot test is shown in Fig. 2.5. As shown, vadose zone piezometer(s) and saturated zone piezometer(s) are co-located to allow sampling of both zones in one location. At Site 1, two SZPs will be installed near the nested VZPs while at Site 2, only one SZP will be installed adjacent to the VZPs. This is due to different depths of existing contamination and controls the depth of air injection in other words, AIWs address contamination in both the shallow and deep groundwater zones at Site 1 and in the shallow groundwater zone only at Site 2. Depth of water monitored by shallow and deep wells as well as depth of the vadose zone are noted in Table 2.1. Based on these data, air will be injected at a depth of approximately 65 and 40 feet below ground surface, at Sites 1 and 2, respectively.

Borehole logs of the wells in the vicinity of the pilot systems indicate that the subsurface materials are comprised of relatively homogeneous sands and gravels. Clay and silt were encountered infrequently, and lenses of these materials were not logged during drilling. Placement of pilot piezometers, therefore, did not require consideration of directional movement of vapors caused by clay lenses. Piezometers were placed at various distances and depths from the AIWs and ASWs to assess ROI and provide adequate sampling locations for representative monitoring of both the saturated and vadose zones during the test.

Pilot testing at both sites was preceded by a mobilization and start-up test period to ensure that on-site equipment was in working order, to prepare drilling contracts, mobilize drillers, install pilot system wells, and obtain pre-characterization samples of soils and groundwater. On-site equipment, including field and laboratory equipment, underwent maintenance checks and was repaired as necessary. Pilot tests began following well installation and pre-characterization sampling and analysis. Pilot testing at Sites 1 and 2 consisted of seven test campaigns: 1) ASW Step Tests, 2) AIW Step Tests, 3) Stabilization Period, 4) Injection of Air (oxygen), 5) Injection of Air and Nutrients (nitrous oxide and triethyl phosphate), 6) Injection of Air, Nutrients, and 4 % Methane, and 7) Post-Test Monitoring.

Step tests for the vadose and saturated zones characterized how the subsurface system responds to air injection and extraction stresses. Baseline conditions were stabilized at anticipated pilot test air injection and extraction rates during the stabilization period. Air injection will determine if concentrations of other organics in the groundwater are sufficient to stimulate biodegradation of chlorinated compounds once oxygen is supplied. Nutrient injection will determine if microbial growth is nutrient limited. Four percent methane will be injected to stimulate methanotrophs in both the saturated and vadose zones. Post-test monitoring will evaluate how the system rebounds following operation of the pilot system. A helium tracer test will be performed following stabilization in Tests 3, 4, and 5 for the assessment of dispersion and diffusion processes in the pilot test area.

ASW Step Tests

Data from ROI step tests at the ASW was used in optimization of ASW operations. The ASW system was optimized such that the presence of volatile contaminants in the blower exhaust and rate of contaminant movement toward the ASW is reduced while still achieving a reasonable area of vapor containment. Optimization in this fashion is intended to increase the time volatile contaminants remain in the vadose zone and the time over which biodegradation occurs. The maximum ROI to be evaluated in these tests is 40 feet. It was anticipated that the vacuum and flow rate required to achieve a 40 foot ROI may not be optimal for biodegradation and that the pilot tests will be required to run at a smaller ROI (i.e., 20 feet). To perform the step tests, the ASW was operated independently of the AIW for 2 days. ROI data obtained under three to four different vacuums and flow rates was used to generate well-specific flow/pressure versus ROI curves. During the step tests, air was extracted from the ASW at an initial flow rate of 5 standard cubic feet per minute (scfm) and increased in 5 scfm increments until a 40 foot ROI was obtained. Pressure were monitored in surrounding VZPs for determination of the ROI.

Table 2.1 Sanitary Landfill Monitoring Well Data

Well Identification	Screen Interval (Feet Above MSL)	Top of Casing (Feet Above MSL)	Approximate Water Table Elevation (Feet Above MSL)	Depth To Water (Feet Below Surface)	D Wells Depth of Water (Feet)	C Wells Depth of Water (Feet)
Site 1						
LFW 38	151.5 - 130.5	170.3	144	26.3	13.5	-
LFW 39	152.2 - 131.2	171.4	144	27.4	12.8	-
LFW 40	152.2 - 131.2	171	144	27.0	12.8	-
LFW 59C	110.3 - 100.3	167.3	144	23.3	-	43.7
LFW 59D	149.3 - 129.3	167.6	144	23.6	14.7	-
LFW 61C	121.1 - 111.0	168.3	144	24.3	-	33.0
LFW 61D	150.4 - 130.3	168.3	144	24.3	13.7	-
Average			144	25.7	13.5	38.3
Site 2						
LFW 48C	118.2 - 108.2	169.3	150	19.3	-	41.8
LFW 48D	155 - 134.9	169.5	150	19.5	15.1	-
LFW 36	151.3 - 130.3	170.4	147	23.4	16.7	-
Average			148.5	21.4	15.9	41.8

Note: MSL - Mean Sea Level

The map displays the LFW65 Well ID area, showing existing wells (LFW44, LFW45, LFW46, LFW47, LFW48, LFW55, LFW36, LFW56, LFW57, LFW37, LFW38, LFW39, LFW40, LFW61, LFW68, LFW67, LFW72, LFW66, LFW71, LFW65, LFW70, LFW69, LFW63, LFW84, LFW10A, LFW22, LFW21, LFW23, LFW42, LFW41) and various features. Key areas include the MAIN SECTION, SOUTHERN EXPANSION, VINYL CHLORIDE BIODEGRADATION PILOT TEST LOCATION (SITE 2), TRICHLOROETHYLENE BIODEGRADATION PILOT TEST LOCATION (SITE 1), HOUSING FOR BLOWER AND COMPRESSOR UNITS, and WETLAND BOUNDARY. Piping is shown connecting the pilot test locations to the housing. A legend indicates that dots represent existing wells and LFW65 is the well ID. A scale bar (0 to 500) and a north arrow are also present.

Figure 2.2 Plan View of Site 1.

Figure 2.3 Plan View of Site 2.

Figure 2.4 Equipment Schematic.

Figure 2.5 Cross-sectional Schematic of the Test Area.

2.3 Equipment and Materials

The equipment utilized for the pilot test system is summarized in Table 2.2 and is described in more detail below. Installed wells (i.e., AIWs, ASWs, VZPs, and SZPs) are summarized in Table 2.3.

2.3.1 Pilot Test Equipment - Vadose Zone

Air Sampling Wells (ASWs): A construction schematic for ASWs is presented in Fig. 2.6. Wells were drilled by hollow stem auguring methods according to the specifications in WSRC 3Q5 Procedures. The 4-inch diameter PVC ASW was drilled to a depth of 2 feet above the groundwater table with a gravel pack extending for 14 feet and a screen interval of 10 feet within the gravel pack. The remaining 10 or 5 feet (Site 1 and Site 2, respectively) was sealed with bentonite grout.

Vadose Zone Piezometers (VZPs): The VZPs bore holes were installed using a hollow stem auguring method per WSRC 3Q5 Procedures. Dual level VZPs were installed in a single bore hole as shown in Fig. 2.7. The VZPs were installed at 10 and 16 feet at Site 1 and Site 2. Dual level VZPs of 1/4-inch stainless steel tubing material were attached to 1" diameter, 2-foot long, 20 slot stainless steel screened sections terminating in 1/4-inch quick-connect fittings. The screened sections were installed in a 3-foot filter sand pack layer at 10 and 16 feet depths at Site 1 and Site 2. The section immediately above the sand packs were sealed with bentonite pellets. The remaining distances (between the lower and upper VZP and between the upper VZP and ground level) were sealed with bentonite chips.

Air Vacuum Blower: A model 22 Roots blower powered by a 240 volt 1.5 horsepower electric motor was attached to each Air Sampling Well. The blower operated at 1725 RPM which produced a 20 SCFM flow at 6 inches of mercury at site 1 and a 15 SCFM flow at 9 inches of mercury at site 2. Power for the blowers was supplied by a portable electric generator at each test site.

2.3.2 Pilot Test Equipment - Saturated Zone

Air Injection Wells (AIWs): Wells were drilled by hollow stem auguring methods according to the specifications in WSRC 3Q5 Procedures. The 2-inch diameter stainless steel AIWs were drilled to depths of 55 and 40 feet below ground surface, for Sites 1 and 2, respectively. Boreholes were screened for 10 feet in the saturated zone. Well screens were installed in fluid sands and did not require any over pack (i.e. gravel, filter sand, etc.) The remaining 45 and 30 feet were sealed with bentonite cement grout for Site 1 and Site 2, respectively (Fig. 2.8).

Saturated Zone Piezometers (SZPs): Wells were drilled by hollow stem auguring methods according to the specifications in WSRC 3Q5 Procedures. SZPs were installed separately in the vicinity of the VZPs. At Site 1, two 2-inch PVC wells were installed to depths of 55 and 40 feet below ground surface with 10-foot screens (top of screens are at 45 and 30 feet below grade surface, respectively). At Site 2, one 2-inch Saturated Zone Piezometer (SZP) was installed in the vicinity of VZPs at a depth of 40 feet below grade. The 10 foot screened interval began 30 feet below ground surface or 10 feet below the average water table level in these wells. All well screens were installed in fluid sands and did not require any over pack (i.e. gravel, filter sand, etc.). Fig. 2.9 depicts a typical SZP.

Air Injection System: A centrally located air injection system serviced both test sites. A diesel driven Atlas-Copco (Holyoke, Ma.) model 100Dd XAS air compressor with a maximum operating pressure of 100 psig and a 340 SCFM capacity supplied a 750 gallon receiver tank manufactured by Wessels Co. (Detroit, Mich.).

The compressor operated at idle speed until the air pressure in the tank dropped below 80 psig. At that point, the compressor charged the tank until the pressure reached 100 psig at which time the compressor returned to the idle mode.

The air receiver tank provides a reservoir of compressed air for the system to draw from thereby reducing the load and cycling requirements placed on the compressor.

A check valve was installed at the outlet of the receiver tank to prevent the accumulation of methane in the receiver tank in the unlikely event the injection system failed to operate correctly.

The outlet of the receiver tank was regulated to 50 psig and supplied air to the individual test sites via stainless steel pipe. The air pressure was further reduced, by a pressure regulator, at each injection site just prior to the line branching to the individual injection lines. This provided individual pressure adjustments for each test site. Given the homogeneity of the subsurface at each test site individual regulators for each injection well was not required.

The minimum size of the air injection system is determined by the requirements of the test site. The equipment described above is much larger than that which was required for the optimization test. The equipment was available for use at no charge to the project and thus was adapted to the optimization test.

Methane Blending System: Due to the small test plot size and the fact that the system would be manned during all nutrient and methane injection phases, a simplified manual injection system was utilized. The methane was supplied via a donated 50,000 standard cubic foot methane tube trailer with a manifolded cylinder supply backup. The methane supply line was routed through a pressure regulator, throttling valve and a flow meter. The outlet of the flow meter was connected to the outlet line from the air receiver tank. The required flow of methane to produce a 4% mixture was calculated and then the flow and pressure adjusted until the correct mixture was obtained. The methane supply line was protected with a pressure relief valve to prevent excess methane from being injected into the line in the unlikely event of the methane regulator failure.

Nutrient Addition System: Compressed nitrous oxide gas (nitrogen source) was added and mixed with the air stream to form a 0.07 % concentration in air. Compressed nitrous oxide was injected in the main header leaving the receiver tank. Flow was monitored and adjusted to assure the correct mixture of gases.

Phosphate was added using the PHOSter process in which an organic phosphorous, triethyl phosphate, is injected into the air stream. The liquid is pumped into the air flow using an infusion pump at approximately 2.4 milliliters per minute (ml/min) or 1 gallon/day. Volatilization of the liquid triethyl phosphate in the air stream results in approximately 0.007 % final gas concentration.

Pressure Gage: Quick disconnects for connection to magnehelic gages were installed at all pressure monitoring points in the air injection/extraction system lines shown in Fig. 2.4. Pressure

transducers were installed at selective VZP to provide constant pressure measurements. Quick connect fittings were attached to gas-tight caps to facilitate attachment of gages and monitoring equipment.

Flow Meter: Orifice plates were installed to monitor flow into the subsurface at each injection well (see Fig. 2.4). During system startup, however, it became evident that the flow into the injection wells was controlled by the back pressure within the well themselves. This back pressure and flow was such that adequate readings could not be generated by the orifice plates. Because of the inability of the orifice plates to measure injection flows, direct reading flow meters were installed in the main supply lines before the individual injection lines. Flows were controlled (i.e. adjusted) on the basis of pressure readings at the wells. During the later part of the test, pitot tubes were installed in the individual inlet lines to each injection well to determine whether injection flows were evenly distributed.

Direct reading flow meters (i.e. manometers) were installed on the outlet of each vacuum blower attached to the Air Sampling Wells.

Figure 2.6 Construction Schematic For Air Sampling Wells.

Figure 2.7 Construction Schematic for Vadose Zone Piezometers.

Figure 2.8 Construction Schematic for Air Injection Wells.

Figure 2.9 Construction Schematic for Saturated Zone Piezometers.

Table 2.2 Equipment List

Air Injection Wells (AIW)	
Total Number (Site 1 and Site 2)	6
Size/Material	2 inch diameter Stainless Steel
Depth (Site 1)	55 feet below grade
Depth (Site 2)	40 feet below grade
Effective Screen Length/Type	10 foot Stainless Steel (Site 1) 10 foot Stainless Steel (Site 2)
Separation Distance	1 set of three wells in a triangular pattern, approximately 35 feet apart
Sparging Pressure (Site 1)	10 - 12 psig
Sparging Pressure (Site 2)	8 - 10 psig
Air Sampling Wells (ASW)	
Total Number (Site 1 and Site 2)	2
Size/Material	4 inch diameter PVC
Depth (Site 1)	Approximately 23 feet below grade
Depth (Site 2)	Approximately 19 feet below grade
Screen Length/Type (Site 1)	10 feet / PVC 20 slot screen
Screen Length/Type (Site 2)	10 feet / PVC 20 slot screen
Location	1 located at center of air injection well triangle
Extraction Rate (Site 1)	Approximately 20 scfm
Extraction Rate (Site 2)	Approximately 15 scfm
Vacuum (Site 1)	Approximately 6 inches of Mercury
Vacuum (Site 2)	Approximately 9 inches of Mercury
Saturated Zone Piezometers (SZP) (Site 1)	
Number	14 Shallow and 14 Deep
Size/Material	2 inch diameter PVC, Shallow and Deep
Depth (Shallow)	Approximately 40 foot below grade
Depth (Deep)	Approximately 55 foot below grade
Length/Type (Shallow)	10 foot screen / PVC
Length/Type (Deep)	10 foot screen / PVC
Saturated Zone Piezometers (SZP) (Site 2)	
Number	14
Size/Material	2 inch diameter PVC
Depth	Approximately 40 foot below grade
Length/Type	10 foot screen / PVC

Table 2.2 Equipment List Continued.

Vadose Zone Piezometers (VZP) (Site 1)	
Number	14 Shallow and 14 Deep
Size/Material	1/4 dia .inch SST Tubing & 1 inch dia. SST Well Screen
Depth (Shallow)	Approximately 10 foot below grade
Depth (Deep)	Approximately 16 foot below grade
Length/Type (Shallow)	2 foot screen/SST
Length/Type (Deep)	2 foot screen/SST
Vadose Zone Piezometers (VZP) (Site 2)	
Number	14 Shallow and 14 Deep
Size/Material	1/4 inch dia. SST Tubing & 1 inch dia. SST Well Screen
Depth (Shallow)	Approximately 10 foot below grade
Depth (Deep)	Approximately 16 foot below grade
Length/Type (Shallow)	2 foot screen/SST
Length/Type (Deep)	2 foot screen/SST
Vapor Sampling System (Site 2 and 2)	
Method	Vacuum
Equipment	Roots Model 22 Vacuum Blower
Piping	1 inch NPT
Apparatus	1 Direct reading Manometer on vacuum exhaust 1 Globe Valve (to control extraction rate) 1 Vacuum Gauge 1 Temperature Gage
Air Injection System	
Method	Compressed Air
Equipment	Atlas Copco Model 100Dd XAS diesel driven air compressor 750 Gallon receiver Tank (Wessels Co.)
Piping	SST Approximately 360 foot to site 1 Approximately 900 foot to site 2
Apparatus	1 Check Valve (@ tank outlet) 3 Pressure regulators (1 @ tank & 1 @ each site.) 8 Ball Valves 9 Pressure Gauges 3 Pitot Tube Flow meters 2 Direct Reading Flow meters (1 @ each site)
Nutrient Injection System	
Methane Injection	
Equipment	1 Methane Gas Trailer, 50,000 SCF with 360 SCF, 9 inch x 55 inch, backup cylinders 1 Methane Regulator 1 Methane Manostat Flow meter
Nitrogen Injection	
Equipment	60 lb @ 745 psig Nitrous Oxide Cylinders (9 inch dia. x 55 inch high) 1 Nitrous Oxide Regulator 1 Nitrous Oxide Manostat Flow meter

Table 2.2 Equipment List Continued.

Phosphate Injection	
Equipment	Triethyl Phosphate, 1 55 gal drum with level indication, in secondary containment 1 High Pressure infusion pump with check valve (to provide required back pressure to pump)
Helium Tracer Injection	
Equipment	292 SCF @2400 psig Helium gas cylinders (9 inch dia. x 55 inch high) 1 Helium Regulator 1 Helium Manostat Flow meter
Power	
Equipment	Each Test Site was serviced by a 240/120 volt diesel powered electrical generator. This generator supplied power for the vacuum blower, sampling equipment, area lighting, etc.
Site Security and Safety	
Both test site were roped off and posted. Safety requirements included the wearing of safety glasses whenever inside the roped areas. The use of hand protection (i.e. rubber gloves) when handling groundwater (sampling, etc.) was required. All personnel reviewed the MSDS sheets for all materials (gases, etc.). Personnel working at the site were either OSHA trained or worked under the supervision of an OSHA trained individual.	

SCF = Standard Cubic Foot

psig = Pounds per square inch gauge

scfm = Standard Cubic Foot Per Minute

SST = Stainless Steel

Table 2.3 Final Well Installation Summary.

	Depth (Feet below Grade)	Length Well Screen (Feet)	Screen Location (Feet below Grade)	Diameter and Material	Number of Wells
Air Injection Wells (AIWs)					
Site 1	55	10	45 to 55	2" Diameter SST	1
Site 2	40	10	30 to 40	2" Diameter SST	1
Air Sampling Wells (ASWs)					
Site 1	20	10	10 to 20	4" PVC	1
Site 2	15	10	5 to 15	4" PVC	1
Saturated Zone Piezometers (SZPs)					
Site 1 Shallow	40	10	30 to 40	2" PVC	14
Site 1 Deep	55	10	45 to 55	2" PVC	14
Site 2	40	10	30 to 40	2" PVC	14
Vadose Zone Piezometers (VZPs)					
Site 1 Shallow	10	2	8 to 10	1" SST Screen With 1/4 " connecting tubing	14
Site 1 Deep	16	2	14 to 16	1" SST Screen With 1/4 " connecting tubing	14
Site 2 Shallow	10	2	8 to 10	1" SST Screen With 1/4 " connecting tubing	14
Site 2 Deep	16	2	14 to 16	1" SST Screen With 1/4 " connecting tubing	14

2.4 Sampling and Analysis

2.4.1 Sampling Objectives

The bioremediation optimization test sampling objective was to provide information on the field applicability of bioremediation and quantitative performance data for input into the design of a biosparging system that is capable of treating the groundwater downgradient of the Sanitary Landfill. Soils, groundwater, and soil vapor was analyzed per Table 2.4. Specific parameter groups (i.e., volatile organics) are defined in Table 2.5.

2.4.2 Sampling Frequency

Sampling frequency and locations as well as individual analyses to be performed are noted in Table 2.4 for each subtest of the overall pilot tests at Sites 1 and 2. Parameter categories noted in Table 2.4 are more fully described in Table 2.5. For instance, the notation, FP-GW in the groundwater column of Table 2.4 indicates that groundwater field parameters will be measured including dissolved oxygen, specific conductance, oxidation-reduction potential (ORP), pH, and water levels.

During pre-characterization, boring logs were recorded for AIWs and ASWs. Soil samples were obtained at 5 ft. increments from these wells for analysis of nutrients, microbial numbers, volatile and semivolatile organics, physical parameters, and other miscellaneous parameters to assess the potential for precipitation and absorption. Following completion of the AIWs and SZPs, water samples were obtained for analysis of nutrients, microbial numbers, organics, field parameters, and miscellaneous parameters in groundwater. Soil gas samples were obtained from VZPs for analysis of carbon dioxide, oxygen, VOCs, and methane.

ROI step tests at the ASWs included measurement of pressure in all SZPs and VZPs, and soil gas field parameters at all VZPs. Flow and total VOCs were also monitored at the sampling ports of both ASWs as well as at the main blower effluent.

During the initial stabilization period (air extraction only), VZPs were monitored for soil gas field parameters; oxygen, carbon dioxide, methane, and VOCs (field measurement). Laboratory VOC measurements were performed regularly. In addition, flow and pressure were monitored in the air extraction system. After startup of the air injection system, groundwater monitoring was added with water levels, dissolved oxygen, VOCs, pressure, and methane concentrations monitored in selective SZPs and flow and pressure monitored at representative points in the air injection system.

During Injection of Air, field parameters were monitored in the groundwater and air at representative SZP, Vadose Zone Piezometer (VZP), and ASW at a frequency of once per day until stabilization. In addition, flow was monitored at the AIW and ASW at the same frequency. At a frequency of once per week, groundwater was collected from representative SZPs for analysis of microbial numbers, nutrient parameters, and laboratory analysis of VOCs. Also at once per week, air samples were collected from the ASW and VZPs for analysis of VOCs.

The above sampling regime continued for, injection of air and nutrients, and the pulsed injection portion of, injection of air, nutrients, and 4% methane. A helium tracer test was performed which included a time dependent gas sampling regiment for the SZPs and VZPs. Pressures and flows were also monitored at these wells. The use of a real time helium analyzer permitted the direct

reading of helium at the individual wells. Problems with support equipment did not permit the conclusion of the test as scheduled. These problems were corrected and the helium tracer test was repeated at the end of the injection campaigns. This will be documented in an addendum to this report.

2.4.3 Sample Equipment and Analysis

A summary of pilot test monitoring from pre-characterization monitoring through the post-test monitoring period is provided in Table 2.4. The following sections present required monitoring equipment, sampling methods, location and schedule of sampling, and analytical methods to be utilized during laboratory analysis of pilot test samples.

Monitoring of pilot tests will involve collecting data on vadose zone pressure, oxygen, carbon dioxide, soil gas chemistry, saturated zone water levels, dissolved oxygen, water chemistry, microbial numbers, and nutrients. Required monitoring equipment has been summarized in Table 2.6. Sample methods are provided in the following section.

Field support included operation of the following instruments at the Sanitary Landfill test site: (1) The Hydrolab Data Sonde 3 multiprobe system which has the capability to measure dissolved oxygen, redox potential, pH, temperature, specific conductivity, and total dissolved solids in groundwater. (2) VOC levels in vadose zone gas were measured using the Photovac portable GC and the Bruel and Kjaer infrared photo-acoustic gas monitor (B&K).

Most data manipulation and analysis was performed using Microsoft Excel 5.0. Well data from the Savannah River Site's Groundwater Monitoring Program was obtained using the Geochemical Information Management System (GIMS) Data Access Module; Graphical Query Language was used for interactive query generation to extract groundwater data from the database. Visualization of 2- and 3-D environmental data was performed using the Silicon Graphics Earth Vision software package running on a UNIX workstation. This program transforms scattered data values into regularly spaced grids with a minimum tension gridding process using a bicubic spline algorithm.

2.4.3.1 Water Sampling

A sampling pump was used to collect groundwater samples from the groundwater monitoring wells according to documented SRS well sampling protocols. Water samples were not required to be filtered in the field. Water levels were monitored with an electric water-level indicator. Field water parameters including dissolved oxygen, oxidation-reduction potential, pH, specific conductivity, and temperature, were monitored using the Hydrolab Surveyor (Hydrolab Inc, Houston, TX) in the field. The Hydrolab Surveyor probes were calibrated as required. All field activities were done in accordance with documented SRS protocols or SRTC Standard Operating Procedures.

2.4.3.2 Soil and Soil Gas Sampling

Subsurface pressures in the vadose zone were monitored at each pressure monitoring point using a quick connect fitting and magnehelic gages.

Gas was collected at all dual level VZP locations for analysis of gas parameters listed in Table 2.5. The following protocol was utilized for sampling gases at the dual level VZP locations. First, a magnehelic gage was attached to the quick connect fitting for measurement of pressure. Second, a high volume pump [approximately 5 liters per minute (l/min)] was attached to the quick connect and the well gas was evacuated until oxygen readings stabilized indicating that one is monitoring soil gas rather than well gases. VOCs were measured in two ways. First, at the screening level, a Photo Ionization Detector (PID) field instrument (Photovac portable GC) was used to estimate total VOCs. Second, samples were collected in 1-liter tedlar bags for direct on-site laboratory analysis. Laboratory VOC analyses will include results for tetrachloroethylene; trichloroethylene; cis-and trans-1,2 dichloroethylene; vinyl chloride; carbon dioxide; and methane.

Soils were collected during well installation for analysis of VOCs, microbial counts, physical parameters, and miscellaneous parameters noted in Table 2.4.

Soils for VOC analysis were collected using a modified syringe tube and plunger and placed in a headspace vial (DSOP 254 and Eddy et al. 1991). Five milliliters of distilled water were added to the vial. The vials were sealed with crimped aluminum rings over teflon-lined septa. Samples were placed in a cooler on ice. Prior to sample analysis, samples were weighed to determine the mass of the sample.

Split spoon samplers were used to collect soil samples for analysis of the physical, miscellaneous, and nutrient parameters noted on Table 2.5. Core specimens for microbial analysis were obtained directly from the split spoon. Cores were sectioned into 3-inch lengths with sterile spatulas and the outermost layer scraped off using a sterile scoopula. The sample were placed in a sterile Whirl-Pak bag and transported to the laboratory on ice for immediate analysis.

Laboratory analyses were performed by personnel at the on-site Savannah River Site laboratory. Laboratory QA/QC were in accordance with the WSRC Quality Assurance Program as outlined in WSRC Management Policies, WSRC-1-01 MP 4.2.

Analytical requirements for nutrients, physical parameters, and miscellaneous parameters are shown in Table 2.7.

Analysis of VOCs, including tetrachloroethylene; trichloroethylene; cis-and trans-1, 2 dichloroethylene; 1,3 dichlorobenzene, 1,4 dichlorobenzene, freon-11, freon 113, carbon tetrachloride, methylene chloride, 1,1,1 trichloroethane, and vinyl chloride, was performed on a Hewlett-Packard 5890 GC. The GC was equipped with an Electron Capture Detector (ECD), an HP 19395A Headspace Sampler, an HP 3392A Networking Integrator, computer-controlled data control and acquisition via Chemstation software, and a 60 meters (m) x 0.75 mm ID Supelco VOCOL wide bore capillary column coated with a 1.5 μ m film. The instrument was calibrated using samples spiked with standard solutions. Within the headspace sampler, the teflon-lined vials are punctured, and the gases were released into the gas chromatograph for analysis by EPA Method Modified 502.2. Methane was analyzed using the above equipment except an Flame Ionizing Detector (FID) replaced the ECD detector.

Total heterotrophic bacteria were enumerated using the aerobic heterotrophic plate count technique that provides an estimate of the total number of viable aerobic and facultatively anaerobic bacteria in the groundwater and soils. Low and high nutrient concentrations of a medium were used to indicate differences in bacteria adapted to oligotrophic and eutrophic conditions. Samples (1 to 3

grams) were weighed directly into 15 milliliters (ml) conical centrifuge tubes containing 9 ml of pyrophosphate buffer. Subsequent serial dilutions were made in FA Buffer. Each dilution (0.1 ml) was inoculated onto a corresponding plate of low and high strength medium of 1 % and full strength formulation of Peptone-Trypticase-Yeast-extract-Glucose (PTYG), respectively (Balkwill 1989). The inoculum was evenly spread over the agar plates and incubated at room temperature for 4 weeks. New colonies were counted each week and added to the previous week's total.

Methanotrophs were enumerated at Site 1 and at Site 2 using the methane enrichment Most Probable Number (MPN) method. Minimal salts media (Fogel et al. 1986) were used with a 10 % methane, 90 % air headspace in Hungate Type Anaerobic Culture tubes sealed with black butyl rubber stoppers. Triplicates of the 3 dilution MPN series were produced for each groundwater sample.

Dichlorobenzene degraders were enumerated at Site 2 and Site 1. This method provided an estimate of the number of viable aerobic and facultatively anaerobic bacteria capable of growth on chlorobenzene as a carbon and energy source. 1-3 g from each sample was diluted in 9 ml pyrophosphate buffered saline. Subsequent serial dilutions were made in FA Buffer. Appropriate dilutions were spread on minimal salts medium solidified with 1.8 % agar (w/v) and supplemented with yeast extract (10 milligram per liter (mg/l)). Chlorobenzene was supplied in the vapor phase to cultures on the solid medium in desiccators at room temperature. Control plates with FA Buffer were incubated in the presence of the chlorobenzene. Plates were incubated for 6-8 weeks or more prior to counting.

Aerobic heterotrophic plate counts provide an estimate of the total number of viable aerobic and facultatively anaerobic bacteria in the groundwater. Low and high nutrient concentrations of a medium were used to indicate differences in bacteria adapted to oligotrophic and eutrophic conditions. Unfixed water samples were diluted in FA Buffer (1:10 v/v) and subsequently diluted in the same buffer. One tenth milliliter of each dilution was inoculated onto a plate of the appropriate medium. For this study, 1 % and full strength formulation of PTYG was used (Balkwill 1989). Sterile techniques were used to spread the inoculum evenly on the surface of the agar. Plates were incubated at room temperature for at least 1 week prior to counting.

Methanotrophic bacteria were counted using the MPN Enumeration method also used for soil samples. Minimal salts media (Fogel et al. 1986) were used with a 10 % methane 90 % air headspace in Hungate Type Anaerobic Culture tubes sealed with black butyl rubber stoppers. Triplicate tubes were run for each dilution. The first dilution contained a 1:10 v/v of sample with two subsequent 1 to 10 dilutions. Tubes were incubated for 8 or more weeks along with a set of 4 control tubes. Headspace methane concentration in the control tubes were averaged and the standard deviation represents the lower limit of methane removal needed to count as a positive tube in the MPNs.

Chlorobenzene degraders were enumerated via the method noted under soils methods except that 0.1 ml of groundwater was utilized for the initial dilution rather than 1-3 grams of soil.

Table 2.4 Sampling Matrix Showing Sample Period, Frequency, Location, Media and Parameters

Sample Period	Soils		Groundwater		Soil Gas	
	Frequency and Location	Parameter Categories	Frequency and Location	Parameter Categories	Frequency and Location	Parameter Categories
Pretest Characterization	ASW, AIW, one SZP & VZP per site	boring logs NUTR, MICR VOCs, PHYS MISC-S	AIW, SZP	NUTR, MICR VOCs, FP-GW MISC-GW	ASW, VZP	FP-SG, VOCs
ASW Radius of Influence Test	-	-	-	-	-	-
AIW Radius of Influence Test	-	-	-	-	VZP	pressure
Stabilization Period (Air Extraction Only)	-	-	-	-	ASW, VZP 1/WK	FP-SG, VOCs
Air Extract/Inject.	-	-	SZP 1/wk 3 wells/site	NUTR, MICR VOCs, FP-GW MISC-GW	ASW, VZP 1/wk	FP-SG, VOCs flow @ ASW
O ₂	-	-	SZP 1/wk 3 wells/site	NUTR, MICR VOCs, FP-GW MISC-GW	ASW, VZP 1/wk	FP-SG, VOCs flow @ asw
O ₂ /Nutrients	-	-	SZP 1/wk 3 wells/site	NUTR, MICR VOCs, FP-GW MISC-GW	ASW, VZP 1/wk	FP-SG, VOCs flow @ ASW
O ₂ /Nutrients/CH ₄	-	-	SZP 1/wk 3 wells/site	NUTR, MICR VOCs, FP-GW MISC-GW	ASW selected VZPS 2/wk	FP-SG, VOCs flow @ ASW
Post-test Sampling	-	-	SZP variable 3 wells/site	NUTR, MICR VOCs, FP-GW MISC-GW	-	-

ASW = Air Sampling Well, AIW = Air-Injection Well, FP-GW = Groundwater Field Parameters, FP-SG = Soil Gas Field Parameters, MICR = Microbial Counts, MISC-GW = Miscellaneous Groundwater Parameters, MISC-S = Miscellaneous Soil Parameters, NUTR = Nutrients, PHYS = Soil Physical Parameters, SZP = Saturated Zone Piezometer, VOCs = Volatile Organic Compounds, VZP = Vadose Zone Piezometer

Table 2.5 Sampling Categories

Parameter Categories	Parameters
Nutrients (NUTR)	Nitrate, Nitrite, Ortho-phosphate
Microbial Numbers (MICRO)	
Volatile Organics (VOCs)	Aerobic heterotrophic bacteria Methanotrophs (Site 1) Chlorobenzene Degraders (Site 2)
Physical Parameters Soils (PHYS)	Grain size analysis Porosity Hydraulic Conductivity Boring logs
Miscellaneous- Soils (MISC-S)	Sulfate
Field Parameters - Groundwater (FP-GW)	Dissolved Oxygen Specific Conductivity Redox Potential pH Water Level
Field Parameters - Soil Gas (FP-SG)	Oxygen Carbon dioxide Methane (Site 1) Chlorobenzene (Site 2) VOCs Pressure Helium

VOC - Volatile Organic Carbon

Table 2.6. Field Monitoring Equipment for Pilot Testing

Gases	
CO ₂ /O ₂ /CH ₄	BNK Infrared Gas Analyzer
VOCs	Flame ionization Detector
Helium	Helium Leak Detector
High Flow Sample Pump	
Groundwater	
Dissolved Oxygen	Hydrolab-Surveyor
Redox Potential	Hydrolab-Surveyor
pH	Hydrolab-Surveyor
Specific Conductivity	Hydrolab-Surveyor
Temperature	Hydrolab-Surveyor
Sampling Pump	Submersible Pump, Munster Simms Engr.
Water Level Indicator	Electronic Indicator
Pressure Gauge	Magnehelic Gauge

CO₂ = Carbon Dioxide

O₂ = Oxygen

CH₄ = Methane

VOC = Volatile Organic Compound

Table 2.7 Laboratory Sample Requirements

Test/Compound	Method	Soil/Groundwater	Sample Container	Holding Time	Sample Preservation
Volatile Organic Compounds	—	S/G	20 ml glass vial, Teflon lined cap	ASAP	Cool, 4 ° C
Nitrate/Nitrite	—	S/G	20 ml glass vial, Teflon lined cap	28 Days	Cool, 4 ° C
Ortho Phosphate	—	S/G	20 ml glass vial, Teflon lined cap	28 Days	Cool, 4 ° C
pH	—	S/G	20 ml glass vial, Teflon lined cap	28 Days	Cool, 4 ° C
Aerobic Heterotrophic Bacteria	—	S/G	50 ml sterile poly vial	—	Cool, dark, <u>do not freeze</u>
Methanotrophic Bacteria	—	S/G	50 ml sterile poly vial	—	Cool, dark, <u>do not freeze</u>
Chlorobenzene Degradors	—	S/G	50 ml sterile poly vial	—	Cool, dark, <u>do not freeze</u>
Soil Grain Size	ASTM D422	S	2" Core Sample	—	N/A
Porosity	—	S	2" Core Sample	—	N/A

2.5 Deviations from the Test Plan

Test No. 1 ASW Step Tests

Due to the extremely high hydraulic conductivity, a 40 foot radius of influence was obtained with extraction values in the range of 10 to 20 scfm and therefore higher extraction rates were not attempted.

Test No. 2 AIW Step Tests

Due to the extremely high hydraulic conductivity, site 1 exhibited a threshold value for air injection of 10 to 12 psig and site 2 exhibited a threshold value of 8 to 10 psig at an injection rate of 15 scfm per site. Flow and pressures above these values exhibited the formation of preferential paths as witnessed by the expulsion of groundwater from neighboring Saturated Zone Piezometers. Therefore, further testing at higher pressures was eliminated.

Test No. 3 Stabilization Period

No deviation

Test No. 4 Injection of Air

The original helium tracer detection equipment intended to be utilized for this test was not available and the use of a substitute detection device (Leekseeker 96) was attempted. The detection level of the Leekseeker 96 is such that the original 0.005 to 0.05% (5 to 500 ppm) helium concentration may produce suspect results. Therefore, a 1% concentration (10,000 ppm) was preferred to ensure adequate results. During the test, the maximum concentration that could be generated by the helium injection system, was 0.65% (6500 ppm). This coupled with strong winds during the test resulted in difficulty in obtaining viable readings. Equipment (test and injection system) modifications have been planned and the helium tracer test was attempted after conclusion of the overall test. This will be documented in our addendum to this report.

Test No. 5 Injection of Air and Nutrients

Due to the problems experienced during the helium tracer test in air only (Test No. 4), the injection of helium was eliminated from this portion of the test.

Test No. 6 Continuous Injection of Air, Nutrients and 4% Methane

Due to the problems experienced during the helium tracer test in air only (Test No. 4), the injection of helium was eliminated from this portion of the test.

The preliminary results of the continuous air only injection phase, showed that continuous injection may not be required. This coupled with the shortage of personnel (for safety reasons continuous injection of methane required continuous surveillance of the test by at least 2 persons) forced the elimination of the continuous air, nutrients and methane portion of this test.

Due to the extremely small flow and pressure threshold values exhibited by the test sites, the injection of air, nutrients and methane without vapor extraction (i.e. shutdown the ASW) was eliminated from this test.

Due to funding and personnel constraints, the collection of soil samples from the vadose zone during injection was eliminated.

Test No. 7 Pulsed Injection of Air, Nutrients and 4% Methane

Due to the preliminary results of the continuous air only injection phase and the shortage of personnel, the pulsed injection campaign was revised to provide injection for 8 hours every other day (i.e., 8 hours on 40 hours off). Additionally, this section of the test was revised to continue air injection and vacuum extraction during those periods when nutrients and methane were not being injected to ensure that the radius of influence was maintained.

Optional Test Injection of Air, Nutrients and 1% Methane

Competitive inhibitions within the microbial communities were not detected and therefore this optional test was not performed.

Test No. 8 Post-Test Monitoring

Due to the extremely slow reduction in microbial activity and the slow rise of contaminant levels after injection was halted, the post test monitoring period has been extended to 3 months.

Field Sampling Plan

Review of the recent local monitoring well data did not exhibit tritium and therefore the analyses for tritium during the Radius of Influence tests were eliminated.

Preliminary analysis results revealed that both test sites were homogeneous both microbially and on the contaminant level. This coupled with the time constraints of collecting samples, the time required to process the samples and the limited personnel available to support the sample preparation and analysis, prompted a revision to the number and frequency of field tests. Results from the pre-test campaign provided the information needed to reduce the number of sample locations. These results showed that well locations 7, 9 and 13 at site 2 and well locations 7S, 7D, 9S, 9D, 13S and 13D at site 1 were representative of the entire respective sites. Thus for the sampling campaigns, only these locations were sampled for VOCs, Hydrolab data and microbial analysis. Additionally, water and gas sample frequencies were changed to a weekly basis.

The existing Sanitary Landfill groundwater monitoring wells either required containerization of the purge water or were administratively restricted from sampling due to suspected mercury content. This prohibited obtaining samples, from these wells, on a regular basis and therefore the additional data and samples that were expected from these wells, could not be obtained.

3.0 Results and Discussion

3.1 Basic Landfill Parameters

Quarterly groundwater monitoring of the landfill shows that the groundwater flow rate and direction, around the landfill has remained southeasterly at a rate of ~47 m/yr (Fig. 1.1). Since the foundation layer for a clay cap was installed over the original and the southern section in the fall of 1994, the water table level has declined significantly underneath the cap causing groundwater to be drawn to the middle of the landfill and then towards the southwest corner (Figs. 3.1, 3.2, and 3.3). A runoff retention basin installed at the same time along the southeast corner of the landfill has focused groundwater flow towards the southwest corner (Fig. 3.3). Outside the landfill the dominant hydrological feature in the area is Upper Three Runs Creek which is approximately 700 m southeast and flows southwest towards the Savannah River. Previous to the cap installation, the leachate from the refuse mass in the landfill moved parallel to the long axis of the landfill. This created a plume of contaminants leaching from the older part of the landfill (Fig. 3.4) along the west side that is dominated by VC (Fig. 1.2) and chlorobenzenes (Fig. 1.5) and another plume along the south side created by contaminants leaching from the newer southern expansion dominated by TCE (Fig. 1.3). The foundation layer of the cap decreased water infiltration enough to pull groundwater towards the center of the landfill on the west side and towards the southwest corner on the south side. This should decrease the size of the plumes outside of the landfill on both sides and focus them towards the southwest corner. A treatment system that intercepts the groundwater at the southwest corner with extensions down the west and south sides of the landfill should be able to intercept all groundwater contaminated by leachate from all parts of the landfill.

The geology of the landfill area is typical of SRS, which is Atlantic Coastal Plain sediments from the late Cretaceous and Tertiary. These sediments consist mainly of unconsolidated interbedded sands, silts and clays. The hydrostratigraphy at the landfill consists of one principal unconfined shallow aquifer, the Steed Pond Aquifer (Figs. 3.5 and 3.6). The Steed Pond Aquifer is 27 m thick at Upper Three Runs Creek and 40 m at the north end of the landfill. For a complete description of the geology and hydrostratigraphy see the RCRA Part B Permit Application (WSRC-IM-91-53). The stratigraphy analyses from boreholes done in this study reveal a vadose zone with a very sandy content (48.3-95.7% sand) with high porosity's and hydraulic conductivity's (Table 3.1). The average hydraulic conductivity in the saturated zone at site 1 was $2.30\text{E-}04$ m/s, while site 2 was $9.97\text{E-}05$ m/s. These hydraulic conductivity values correlate well with the values presented by Freeze and Cherry (1979) and Sowers (1979) for similar sediments. In addition, the estimated hydraulic conductivity values also correlate well with the values obtained for the 1994 field permeability testing of the "D" level wells at the Sanitary Landfill. The lowest recommended hydraulic conductivity for biostimulation using liquid nutrient injection is $10\text{E-}06$ m/s and for gaseous nutrient injection or extraction $10\text{E-}11$ m/s (Baker and Herson, 1990). Since both sites were well above these limits, biosparging should not be physically restrained on either side of the landfill.

Figure 3.1 Water Table Piezometric Map of SRS Landfill for Third Quarter 1994.

Figure 3.2 Water Table Piezometric Map of SRS Landfill for First Quarter 1995.

Figure 3.3 Water Table Piezometric Map of SRS Landfill for Fourth Quarter 1995.

Figure 3.4 SRS Landfill Map of Cells and the Years Filled.

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Figure 3.6 Lithological Cross-Sectional Map of the West Side of the SRS Sanitary Landfill.

Table 3.1 Physical Characteristics of Sediment at Sites 1 and 2.

	Depth Below Grade (ft)	% Gravel	% Sand	% Silt	% Clay	Porosity Coefficient	Estimated Hydraulic Conductivity (m/s)
Site 1	1 - 2	0	88	7.1	4.9	0.3005	1.47E-04
	6 - 7	5.4	72.6	6.5	15.5	0.255	4.71E-07
	10 - 11	0.6	52.2	8.6	38.6	0.255	1.54E-09
	16 - 17	0	48.3	31.4	20.3	0.2611	8.64E-08
	22 - 23*	0	95.7	3.6	0.7	0.4419	2.30E-03
Site 2	0 - 1	0	71	10.9	18.1	0.255	1.54E-07
	2 - 3	0	85.2	10.7	4.1	0.2728	1.45E-04
	8 - 9	13.3	63.1	13.4	10.2	0.255	1.78E-05
	20 - 21	0	73.6	14.8	11.6	0.255	8.65E-06
	24 - 25*	0	91	5.4	3.6	0.371	9.97E-04

* = saturated zone.

3.2 Experimental Campaigns at Site 1

The pretest stabilization and monitoring began on 6/27/95 (Table 3.2). This was followed by the radius of influence step test which began 7/11/95 and then the air injection/extraction test on 7/18/95. The compressor failed on 8/8/95, thus stopping all injection and extraction until 9/11/95. The air injection and extraction resumed on 9/11/95. On 9/15/95 a Helium tracer test was begun and stopped after 1 day due to equipment problems. Nitrous oxide injection began on 9/18/95 and continued for 3 cycles (8 h of injection followed by 40 h of air alone). The site 2 flow meter failed, so system was shut down for repairs on 9/23/95. Air injection was restarted on 10/5/95, nitrous oxide and triethyl phosphate were added to the injection system for 7 cycles beginning 10/6/95. Methane was added to the injection stream for 7 cycles on 10/20/95. The injection/extraction system was stopped on 11/1/95. From 11/2/95 to 3/1/96 no injection or extraction was done at the site.

Table 3.2 Test Campaigns for the In Situ Bioremediation Optimization Test by Site.

Test Phase	Site 1		Site 2	
	Begin Test	End Test	Begin Test	End Test
Pretest Stabilization	6/27/95	7/10/95	6/27/95	7/10/95
Radius of Influence Step Test	7/11/95	7/18/95	7/12/95	7/18/95
Air Injection with Vacuum Extraction (1)	7/11/95	8/8/95	7/11/95	8/8/95
No air, No Vacuum, Sampling Continued	8/9/95	9/10/95	8/9/95	9/10/95
Air Injection with Vacuum Extraction	9/11/95	9/17/95	9/11/95	9/17/95
Helium Tracer Test (2)	9/15/95	9/16/95	9/15/95	9/16/95
Air Injection, Vacuum Extraction & N ₂ O Injection (3)	9/18/95	9/22/95	9/18/95	9/22/95
No air, No Vacuum, Sampling Continued (4)	9/23/95	10/4/95	9/23/95	10/4/95
Air Injection with Vacuum Extraction	10/5/95	10/6/95	10/5/95	10/6/95
Air Injection, Vacuum Extraction, TEP & N ₂ O Injection (5)	10/6/95	10/19/95	10/6/95	10/19/95
Air Injection, Vacuum Extraction, TEP, Methane & N ₂ O Injection (6)	10/20/95	11/1/95	(7)	(7)
No air, No Vacuum, Sampling Continued (1)	11/2/95	3/1/96	10/20/95	3/1/96
(1) - Air Compressor failed.				
(2) - Test not completed. Problems with helium injection system and test equipment				
(3) - N ₂ O injected for 3 cycles. One cycle equals 8 hours N ₂ O with air injection followed by 40 hours air injection alone. Read wrong flow meter ball injected less than required percentage.				
(4) - Flow meter failed @ site 2. Shut system down for repairs and PM of compressor and vacuum blowers.				
(5) - NO ₂ & TEP injected for 7 cycles. One cycle equals 8 hours N ₂ O & TEP with air injection followed by 40 hours air injection alone. First injection cycle had problem with TEP pump not pumping. Corrected for 2nd cycle.				
(6) - Methane, N ₂ O & TEP injected for 7 cycles. One cycle equals 8 hours Methane, N ₂ O & TEP with air injection followed by 40 hours air injection alone.				
(7) - Site 2 did not require methane injection. Since methane could not be selectively injected to site 1 alone, all injection to site 2 was ceased during methane injection. Sampling of site 2 continued.				

3.2.1 Physical Parameters

The lithology of this site was mostly sand (>48%) with a zone of higher clay content at 10-11 ft. (Table 3.1). The hydraulic conductivity for all sediments was $>1.54\text{E-}09$ m/s and the saturated zone was $>2.30\text{E-}03$ m/s. Since hydraulic conductivity's need to be less than $10\text{E-}11$ to impede air flow and less than $10\text{E-}06$ to impede liquid flow this area can be characterized as being relatively porous with no lithological impediments to biostimulation. The drilling report characterizes the saturated zone as fluid sands (CDM Federal, 1995).

The radius of influence test (ROI) showed that the deepest part of the unsaturated zone and capillary fringe zone (14-16 ft.) was equally permeable in all directions since pressure decreased with distance incrementally from any of the three injection wells (Figs. 3.7, 3.8, 3.9, 3.10). Pressure drops over distance show a 50% decrease in the first 6 ft. or less, 50% of this pressure being lost in the next 15 ft. and 50% of this final pressure being lost in the next 30 ft. The ROI was observed to continue in the all three injection tests to the farthest piezometer measurable, ie. 54 ft. The shallow piezometer pressures showed a great deal of variability depending on the orientation to the injection well being used. Since these wells were screened at 9-10 ft. this suggests either that the clayey sediments encountered at 10-11 ft. may be discontinuous or that the screens were placed slightly above this clayey area. The later explanation is preferred since all the drilling logs indicated the same lithology. In general, the shallow piezometers, like the deep piezometers, also showed that areas as far as 54 ft away from the injection well could be effected. Those wells showing minimal pressure increases were VZP-10, 11, 9, and 5. Since these 4 wells showed the same effect no matter which well was used for injection (Figs. 3.7, 3.8, 3.9) or when all 3 injection wells were on (Fig. 3.10), this provides further evidence that the screens of these wells were above the clayey unit, since air flow was impeded even when the closest well was used for injection AIW-1 (Fig. 3.7). These wells would also be expected to show less changes, at least initially, in chemical composition in the soil gas than the other wells.

The temperature of the groundwater in this area is typically 19°C and varies less than 2°C either up or down through out the year.

Figure 3.7 Pressure at Site 1 Vadose Zone Piezometers by Distance During Injection at AIW-1.

Figure 3.8 Pressure at Site 1 Vadose Zone Piezometers by Distance During Injection at AIW-2.

Figure 3.9 Pressure at Site 1 Vadose Zone Piezometers by Distance During Injection at AIW-3.

Figure 3.10 Pressure at Site 1 Vadose Zone Piezometers by Well During Injection In All Three AIW Wells (1-3).

3.2.2 Chemical Parameters

The sediment chloride, nitrite, nitrate, phosphate, and sulfate were less than 1 ppm with the exception of sulfate which reached 4 ppm at 5 ft. (Table 3.3). These levels are generally low and typical of sediments that have not been severely impacted by leachates.

Table 3.3 Sediment inorganic chemical concentrations by depth for sites 1 and 2.

Depth (ft)	Site	Chloride (ppm)	Nitrite (ppm)	Nitrate (ppm)	Phosphate (ppm)	Sulfate (ppm)
5	1	<0.325	< 0.1	<0.359	ND	4.137
10	1	<0.500	< 0.1	<0.542	ND	<1.025
15	1	0.762	< 0.1	<0.253	ND	< 0.1
20	1	<0.506	< 0.1	<0.153	ND	< 0.1
22-25	1	<0.931	< 0.1	<0.166	ND	< 0.1
5	2	0.338	< 0.1	< 0.1	< 0.1	2.417
10	2	0.560	ND	ND	ND	1.191
15	2	1.281	ND	< 0.1	ND	< 0.1
20	2	6.045	ND	< 0.1	ND	< 0.1
25	2	4.041	< 0.1	< 0.1	ND	< 0.1

ND = Not Detected, Detection Limit = 0.1 ppm

The pH of the groundwater at Site 1 ranged from 4.02-6.26 with a average of 4.89 (Fig. 3.11). This is typical of groundwater in the area and at the Savannah River Site. The shallow wells showed greater variability than the deeper wells. Biostimulation could alter the pH slightly in poorly buffered groundwater; however, the differences observed were not significant until nitrous oxide addition was started. After nitrous oxide addition all wells increased in pH with well 9S showing the greatest increase.

Total organic carbon (TOC) concentrations from nearby monitoring wells (LFW 38 and LFW 59) range from 200-2700 ppm. Since background TOC for the area is normally <1000 ppm, the groundwater data suggests some leachate impact from the landfill.

Dissolved oxygen was <20% for all wells before injection started. After injection started all wells showed significant increases in DO ($F=3.4$, $P<0.007$), with the shallow wells reaching supersaturation, ie. >100% (Fig. 3.12). Differences between wells were not significant. This suggests that the air injection was reaching all wells but was having the greatest effect on the shallow wells. Most of the wells were able to maintain the DO for 2-3 weeks. This suggests that this area has some bioactivity, but it is not sufficient to deplete the groundwater oxygen to completely anaerobic conditions like other parts of the landfill. The lower TOC for this site compared to other areas of the landfill also suggests a smaller carbon/energy source to support high intrinsic bioactivity. The Redox Potential changes also support the picture of an aerobic or microaerophilic environment that air injection will increase bioactivity only slightly (Fig. 3.13). Differences were significant by well ($F=5.1$, $P<0.001$) and campaign ($F= 3.6$, $P<0.005$). The redox potential followed a trend similar to DO and was between 350 and 700 mV for all wells. If the groundwater had high bioactivity and the oxygen had been completely used up, the redox potential would have been very low and/or negative.

The specific conductance of the groundwater at site 1 ranged from 0.02 to 0.650 mS/cm (Fig. 3.14). The changes observed during the different injection campaigns were insignificant and the deeper wells were only slightly lower in conductivity than the shallow wells.

The concentration for nitrate in the groundwater was generally very low <1 ppm; however the deeper wells varied from less than 1 ppm to >7 ppm (Figs. 3.15 and 3.16). Differences were very significant by well ($F=47.0$, $P<0.00001$) but not by campaign. The variability in the deeper wells was not significantly effected by the campaigns. The shallow wells which were the most depleted of nitrate, had the highest recorded concentrations during nitrous oxide injection. This would suggest that nitrate concentration is limiting for bioactivity at this site and the nitrous oxide can provide an additional source of nitrate.

Nitrite was very low in the groundwater and was detected only when the air was not being injected or nitrous oxide was being injected (Figs. 3.17 and 3.18). Differences were significant by well ($F=2.5$, $P<0.05$) and campaign ($F=9.0$, $P<0.00001$). Since nitrite does not accumulate under aerobic conditions, this suggests that the groundwater is intrinsic microaerophilic and that nitrous oxide injection is stimulating nitrogen transformation. Both the deep wells and shallow wells at this site showed a similar pattern; however, the deeper wells had a significantly lower range in nitrite than the shallow wells. This further suggests that the deep wells were lower in bioactivity than the shallow wells since nitrite is intermediary product in denitrification and nitrification.

Chloride in the groundwater was highest in the shallow wells reaching concentrations as high as 60 ppm in well 9S (Figs. 3.19 and 3.20). Since chloride is produced by aerobic breakdown of chlorinated solvents areas with higher bioactivity would be expected to have resulting higher chloride. Chloride concentrations were highest in 9S which also exhibited the greatest bioactivity. Differences between wells were significant ($F=18.1$, $P<0.00001$). The variability prevented significant trends from being observed between campaigns.

TCE in the groundwater declined to <5 µg/l during the methane and nutrient injection campaign in all wells except 2 of the deep wells (Figs. 3.21 and 3.22). Differences were significant by well ($F=5.8$, $P<0.001$) and campaign ($F=3.2$, $P<0.02$). The concentrations slowly increased to pre-injection levels after 3-5 weeks. During periods of no injection, TCE concentrations were at their highest. Given the higher aerobic bioactivity that the inorganic parameters indicated during biostimulation campaigns, the result was biodegradation of TCE.

A similar pattern was also observed for chlorobenzene at this site (Figs. 3.23 and 3.24). Differences were very significant by campaign ($F=9.6$, $P<0.00001$). After the first biostimulation campaign with nitrous oxide and TEP alone, chlorobenzene was reduced to non detect, ie. <5 µg/l. Five months after this biostimulation, chlorobenzene was still not detectable in any of the shallow or deep wells at site 1. An identical pattern was observed for 1, 4 dichlorobenzene (Figs. 3.25 and 3.26). Differences were significant by well ($F=5.4$, $P<0.002$) and campaign ($F=10.3$, $P<0.0001$). The contaminant disappearance pattern during the operating campaigns would indicate that air alone may be sufficient to degrade the chlorobenzenes present; however, air plus nitrous oxide, TEP and methane is necessary to biodegrade the TCE at this site.

The presence of TCE at this site provides further evidence of the aerobic or microaerophilic nature of the site and the lack of sufficient carbon to support an anaerobic community. If anaerobic conditions were persistent at this site, then TCE would have been reductively dechlorinated to dichloroethylene or vinyl chloride which may then accumulate. No VC was detectable at this site,

only TCE and small amounts of PCE. The contaminant concentrations in the vadose zone also went to non detectable levels detect for all contaminants except PCE after biostimulation was started (see Appendix A for vadose zone contaminant data). PCE concentrations went down significantly but were measurable after the last operating campaign. Chloroform, carbon tetrachloride, 1,1,1 TCA, and TCE were all reduced to $<5 \mu\text{g/l}$ after biostimulation. The highest concentrations were observed during the periods of no air injection prior to the last biostimulation with methane in all piezometers and depths. All soil gas contaminants except PCE continue to be undetectable 3-4 months after the methane biostimulation. This shows that biostimulation with methane provides biodegradation to a wide variety of VOC contaminants and stimulates the environment for an extended period of time.

Figure 3.11 pH by Well during Operating Campaigns at Site 1.

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Figure 3.12 Dissolved Oxygen Saturation by Well during Operating Campaigns at Site 1.

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Figure 3.13 Redox Potential by Well during Operating Campaigns at Site 1.

+ Figure 3.14 Conductivity by Well during Operating Campaigns at Site 1.

+ Figure 3.15 Nitrate for Shallow Wells during Operating Campaigns at Site 1.

Figure 3.16 Nitrate for Deep Wells during Operating Campaigns at Site 1.

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Figure 3.17 Nitrite for Shallow Wells during Operating Campaigns at Site 1

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Figure 3.18 Nitrite for Deep Wells during Operating Campaigns at Site 1.

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Figure 3.19 Chloride for Shallow Wells during Operating Campaigns at Site 1.

+ Figure 3.20 Chloride for Deep Wells during Operating Campaigns at Site 1.

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Figure 3.21 Trichloroethylene for Shallow Wells during Operating Campaigns at Site 1.

Figure 3.22 Trichloroethylene for Deep Wells during Operating Campaigns at Site 1.

+ Figure 3.23 Chlorobenzene for Shallow Wells during Operating Campaigns at Site 1.

+ Figure 3.24 Chlorobenzene for Deep Wells during Operating Campaigns at Site 1.

+ Figure 3.25 1, 4 Dichlorobenzene for Shallow Wells during Operating Campaigns at Site 1.

+ Figure 3.26 1, 4 Dichlorobenzene for Deep Wells during Operating Campaigns at Site 1.

3.2.3 Microbiological Parameters

The in situ respiration test demonstrated that the normal 20% DO saturation could be increased to 95% in less than 5 h (Fig. 3.27). After the air injection was stopped the % saturation decreased back to the ambient 20% in about 5 h. The ability of the injection system to achieve 95% saturation in a couple of hours suggest that biological oxygen demand at this site is low. This coincides with the levels of TOC observed; however, the biological oxygen demand is sufficient to use the extra DO within 5 hours after sparging stops.

Densities of methanotrophs were higher in the deeper wells, though well 9 had high methanotroph densities in both the shallow and deep zones (Figs. 3.28). The air injection alone stimulated the methanotrophs only slightly; however, the multiple nutrient with methane injection campaign stimulated all wells except 13D. Even those wells that were barely detectable (7S and 13S) began to increase after methane injection. This data suggests that the deeper wells may have a better source of intrinsic methane than the shallow wells, but that all areas will respond to methane pulses. Decreases in contaminants were concomitant with increases in densities of methanotrophs.

Densities of chlorobenzene-degraders were significantly different by both well ($F=9.6$, $P<0.0001$) and campaign ($F=3.0$, $P<0.02$). CB-degrader counts were barely detectable prior to air injection; however, after air injection began densities increased two orders of magnitude and increased an additional two orders of magnitude after air and nutrient injection were started (Figs 3.29 and 3.30). Densities in both the shallow and deep wells decreased slowly after injection was stopped.

Figure 3.27 In Situ Respiration Test at Site 1.

+ Figure 3.28 Densities of Methanotrophs in the shallow and deep wells over time at Site 1.

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Figure 3.29 Densities of Chlorobenzene-degraders in the shallow wells over time at Site 1.

+ Figure 3.30 Densities of Chlorobenzene-degraders in the deep wells over time at Site 1.

3.3 Experimental Campaigns Site 2

The pretest stabilization and monitoring began on 6/27/95 (Table 3.2). This was followed by the radius of influence step test which began 7/11/95 and then the air injection/extraction test on 7/18/95. The compressor failed on 8/8/95, thus stopping all injection and extraction until 9/11/95. The air injection and extraction resumed on 9/11/95. On 9/15/95 a Helium tracer test was begun and stopped after 1 day due to equipment problems. Nitrous oxide injection began on 9/18/95 and continued for 3 cycles (8 h of injection followed by 40 h of air alone). The flow meter failed, so system was shut down for repairs on 9/23/95. Air injection was restarted on 10/5/95, nitrous oxide and triethyl phosphate were added to the injection system for 7 cycles beginning 10/6/95. Unlike site 1, methane was not added to the injection stream, therefore injection and extraction was stopped on 10/19/95. From 10/20/95 to 3/1/95 no injection or extraction was done at this site.

3.3.1 Physical Parameters

The lithology of this site is sand (>63%) with no low permeability areas (Table 3.1). The hydraulic conductivity for all sediments was $>1.54\text{E-}07$ m/s and the saturated zone was $>9.970\text{E-}04$ m/s. Since hydraulic conductivity's need to be less than $10\text{E-}11$ to impede air flow and less than $10\text{E-}06$ to impede liquid flow this area can be characterized as being relatively porous with no lithological impediments to biostimulation. The drilling report characterizes the saturated zone as fluid sands.

The radius of influence test (ROI) showed that the deepest part of the unsaturated zone and capillary fringe zone (14-16 ft.) was equally permeable in all directions since pressure decreased with distance incrementally from any of the three injection wells (Figs. 3.31, 3.32, 3.33, 3.34). Pressure drops over distance show a 50% decrease over 40 ft. The ROI was observed to continue in all three injection tests to the farthest piezometer measurable, ie. 54 ft. The shallow piezometer pressures showed a similar pattern of pressure decrease for each injection test, indicating no impermeable zones or piezometers that were screened above an less permeable strata. In general the shallow piezometers, like the deep piezometers also showed that areas as far as 54 ft away from the injection well could be effected.

The temperature of the groundwater in this area is typically 19°C and varies less than 2°C either up or down through out the year.

Figure 3.31 Pressure at Site 2 Vados Zone Piezometers by Distance During Injection at AIW-1.

Figure 3.32 Pressure at Site 2 Vadose Zone Piezometers by Distance During Injection at AIW-2.

Figure 3.33 Pressure at Site 2 Vadose Zone Piezometers by Distance During Injection at AIW-3.

Figure 3.34 Pressure at Site 2 Vadose Zone Piezometers by Well During Injection In All Three AIW Wells (1-3).

3.3.2 Chemical Parameters

The sediment nitrite, nitrate, phosphate, and sulfate were less than 1 ppm with the exception of sulfate which reached 2.4 ppm at 5 ft. (Table 3.2). These levels are generally low and typical of sediments that have not been severely impacted by leachates. However, the saturated zone concentrations of chloride are much higher than ambient, 6 ppm, and indicate leachate impact and possibly biodegradation of chlorinated solvents, since chloride is the end product of aerobic oxidation of these contaminants.

The pH of the groundwater at site 2 ranged from 6.4 to 6.8 with a average of 6.6 (Fig. 3.35). This is more basic than is typical of groundwater in the area and at the Savannah River Site and may be indicative of contamination. The wells showed little variability. Biostimulation could alter the pH slightly in poorly buffered groundwater; however, the differences observed were not significant.

Total organic carbon (TOC) concentrations from nearby monitoring wells (LFW 8 and LFW 48) range from 3900-8420 ppm. Since background TOC for the area is normally <1000 ppm, the groundwater data suggests that this site receives significant leachate impact from the landfill.

Dissolved oxygen was <2% for all wells before injection started. After injection started, all wells showed increases in DO; however, since these increases were only to 10 % saturation, they were not significant (Fig. 3.36). Differences between wells and campaigns were not significant. From other parameters and tests, eg. nitrite, in situ respiration, we know that oxygen was being utilized rapidly. This suggests that this area has high bioactivity that is sufficient to deplete the groundwater oxygen to completely anaerobic conditions like other parts of the landfill. The high TOC for this site compared to other areas of the landfill also suggests a large carbon/energy source to support high intrinsic bioactivity. The Redox Potential changes also support the picture of an anaerobic environment and that air injection alone will significantly increase bioactivity (Fig. 3.37). Differences were not significant by well, but were very significantly different by campaign ($F=7.0$, $P<0.0001$). The redox potential was between -70 and 135 mV for all wells. When the groundwater has high bioactivity and the oxygen has been completely consumed, the redox potential would be very low and/or negative. This is what was observed during the operating campaigns, ie. when air was being injected the redox shifted to positive but when no air was being injected anaerobic conditions prevailed allowing negative redox conditions to be reached.

The specific conductance of the groundwater at Site 2 ranged from 0.02 to 0.580 mS/cm (Fig. 3.38). The changes observed during the different injection campaigns were insignificant and though well 9 always had a higher conductivity than the other 2 wells..

The concentration for nitrate in the groundwater was generally very low <1 ppm. Differences were not significant by campaign or well. This would suggest that nitrate concentration is limiting for bioactivity at this site and the nitrous oxide can provide an additional source of nitrate. Nitrite was very low in the groundwater and was detected only when the air was not being injected or nitrous oxide was being injected (Fig. 3.39). Differences were not significant by well, but were very significant by campaign ($F=30.80$, $P<0.00001$). Since nitrite does not accumulate under aerobic conditions, this suggests that the groundwater is intrinsically anaerobic and that nitrous oxide injection is stimulating nitrogen transformation. Since nitrite is intermediary product in denitrification and nitrification, its detection during periods of biostimulation suggest higher bioactivities in the groundwater at those times.

Chloride in the groundwater was highest in well 9 reaching concentrations as high as 55 ppm (Fig. 3.40). Since chloride is produced by aerobic breakdown of chlorinated solvents areas with higher bioactivity would be expected to have resulting higher chloride. Chloride concentrations were highest in 9 which also exhibited the greatest bioactivity, and the differences between wells were significant ($F=32.8$, $P<0.00001$). At Site 2, a factorial analysis of variance (FANOVA) showed that while the specific campaigns were not statistically different from one another, the campaigns in which air was injected had significantly higher chloride levels than the campaigns in which air was not injected.

VC in the groundwater declined to $<5 \mu\text{g/l}$ during the first air injection campaign in all wells (Fig. 3.41). Differences were significant by well ($F=3.9$, $P<0.05$) and campaign ($F=201$, $P<0.00001$). Well 9 showed the greatest changes. After 5 months, the VC concentrations have still not exceeded $12 \mu\text{g/l}$. During periods of no injection, VC concentrations were at their highest. Given the higher aerobic bioactivity that the inorganic parameters indicated during biostimulation campaigns, the result was biodegradation of VC.

A similar pattern was also observed for chlorobenzene at this site (Fig. 3.42). Differences were very significant by campaign ($F=17.3$, $P<0.00001$). After the biostimulation campaign with air alone, nitrous oxide and TEP, chlorobenzene was reduced to non detect, ie. $<5 \mu\text{g/l}$. Five months after this biostimulation chlorobenzene was still not detectable in any of the wells at site 2. An identical pattern was observed for 1, 4 dichlorobenzene (Fig. 3.43). Differences were significant by well ($F=8.0$, $P<0.008$) and campaign ($F=5.25$, $P<0.01$). The contaminant disappearance pattern during the operating campaigns would indicate that air alone may be sufficient to degrade the chlorobenzenes present; however, air plus nitrous oxide, and TEP will biostimulate complete degradation of all contaminants at this site.

The presence of VC at this site provides further evidence of the anaerobic nature of the site and the abundance of carbon to support an anaerobic community. Since anaerobic conditions were persistent at this site, TCE and PCE were reductively dechlorinated to vinyl chloride which then accumulates. The contaminant concentrations in the vadose zone also went to non detectable levels for all contaminants except PCE after biostimulation was started (see Appendix A for vadose zone contaminant data). PCE concentrations went down significantly, but were measurable after the last operating campaign. Chloroform, carbon tetrachloride, 1,1,1 TCA, and TCE were all reduced to $<5 \mu\text{g/l}$ after biostimulation. The highest concentrations were observed during the periods of no air injection prior to the last biostimulation with methane, in all piezometers and depths. All soil gas contaminants, except PCE, continue to be undetectable 3-4 months after the air/nutrient biostimulation. This shows that biostimulation with air/nutrients provides biodegradation to a wide variety of VOC contaminants and stimulates the environment for an extended period of time.

Figure 3.35 pH by Well during Operating Campaigns at Site 2.

Figure 3.36 Dissolved Oxygen Saturation by Well during Operating Campaigns at Site 2.

Figure 3.37 Redox Potential by Well during Operating Campaigns at Site 2.

Figure 3.38 Conductivity by Well during Operating Campaigns at Site 2.

Figure 3.39 Nitrite by Wells during Operating Campaigns at Site 2.

Figure 3.40 Chloride by Wells during Operating Campaigns at Site 2.

Figure 3.41 Vinyl Chloride by Wells during Operating Campaigns at Site 2.

Figure 3.42 Chlorobenzene by Wells during Operating Campaigns at Site 2

Figure 3.43 1, 4 Dichlorobenzene by Wells during Operating Campaigns at Site 2.

3.3.3 Microbiological Parameters

The in situ respiration test showed that air injection could increase the DO to only 25% saturation from the background level that was normally less than 10% (Fig. 3.44). This suggests that this site has a very high biological oxygen demand, which fits with the high TOC concentrations and the higher densities of contaminant-degraders.

Densities of methanotrophs were high intrinsically (Fig. 3.45). The air injection alone stimulated the methanotrophs only slightly; however, the multiple nutrient injection campaign seemed to decrease the densities of methanotrophs. This data suggests that as intrinsic sources of methane are utilized faster by the aerobic conditions created by air injection that methane depletion could inhibit the methanotrophs. The implications are that long pulse intervals or methane additions may also be necessary at this site in the future.

Densities of chlorobenzene-degraders were significantly different by campaign ($F=6.8$, $P<0.005$) but not by well. CB-degrader counts were low (<500 cells/ml) prior to air injection; however, this intrinsic density suggests previous stimulation from intrinsic sources and a adapted community. After air injection began, densities increased two orders of magnitude and increased an additional two orders of magnitude after air and nutrient injection were started (Fig. 3.46). After the last injection campaign CB-degrader densities remained high for at least 3 months. This accounts for the disappearance of all contaminants at site 2 for this same 3 month period.

Figure 3.44 In Situ Respiration Test for Site 2.

Figure 3.45 Densities of Methanotrophs by well over time at Site 2.

Figure 3.46 Densities of Chlorobenzene-degraders by well over time at Site 2.

3.4 Comparison of Sites

The two sites were very different for many chemical and microbiological parameters. The root cause of this difference is that groundwater at each site receives leachate from different parts of the landfill. Since groundwater flows parallel to the long axis of the landfill, Site 2 which is midway down the west side, receives leachate contamination from a larger and older part of the landfill. Site 1, in the middle of the south side, has the newer southeast corner of the southern expansion of the landfill as its principal source of leachate. Thus, Site 2 has higher concentrations of organic carbon, lower dissolved oxygen, more reduced contaminants, produces more methane intrinsically, and has higher microbial activity than Site 1. Thus Site 1 will require more nutrients to stimulate biological activity to the same level as Site 2. The operating campaigns support this hypothesis.

The two sites were similar in that they have relatively high hydraulic conductivities that allow injection of air at relatively low pressures to provide a wide radius of influence. Both sites had depressed oxygen levels in the groundwater due to biological oxygen demand; however, the oxygen consumption rate at site 2 was several times greater than site 1.

Evidence for Biodegradation of Chlorinated Solvents for the Two Landfill Test Sites

The following are evidence for biodegradation of trichloroethylene and/or vinyl chloride:

- 1 Increase in populations of degrading organisms (i.e., methanotrophs and chlorobenzene degraders).
- 2 Production of chloride in the saturated zone, pH decrease.
- 3 Reduction in the mass of contaminants in the saturated and unsaturated zones after stimulation of indigenous organisms.

These are the accepted criteria for biodegradation evidence (National Research Council, 1994).

4.0 Conclusions and Recommendations

The primary objective of the optimization test was to determine the optimum design parameters for full-scale operation of a in situ bioremediation system to treat groundwater at the SRS sanitary landfill. The following conclusions were made from this optimization test:

1. Lithology and hydrology on both the southern and western sides of the sanitary landfill will support air and gaseous nutrient injection for in situ bioremediation. An unexpected finding was that pressures needed to biosparge (6-10 psig) were much lower than originally expected. The hydraulic conductivity was $> 10E-05$ m/s in all areas, the minimum for air injection is $10E-11$ m/s.
2. The two test sites and their associated sides of the landfill exhibit significant differences in terms of ambient dissolved oxygen concentrations, total organics, anaerobic vs. aerobic bioactivity, total community bioactivity, and types of contaminants of concern. All of these differences are due to the age of the source refuse mass that is creating the leachate for these two areas. The west side of the landfill is dominated by leachate from the oldest part of the landfill, while the south side is dominated by leachate from the southern expansion which was filled last. The older parts of the landfill have more leachable components creating more bioactivity and therefore higher oxygen consumption rates, more fermentation products (including contaminant daughter products eg. VC), and generally more types of contaminants.
3. Stripping of the COCs from the water phase to the air phase by the injection process was found to be insignificant at either test site. COC's in the groundwater did not change significantly in response to air injection alone at the southern site where bioactivity could not be stimulated by air alone.
4. In situ biostimulation with injection of air and gaseous nutrients was effective at both sites and could reduce the concentrations of COCs to undetectable levels in the groundwater and vadose zone, i.e. < 2 ppb. Indigenous microbes capable of degrading the contaminants increased immediately with gas biostimulation and began degrading the ambient COCs. This degradation was complete as evidenced by the concomitant increase in chloride in the same area. An unexpected finding was the resiliency of the microbial population once it had been stimulated. After the injection was stopped at both sites the microbial populations came down slowly, causing the contaminant levels to rise slowly also. This demonstrated that a single injection pulse on a weekly or monthly basis may be all that is necessary to maintain complete bioremediation of COCs at both sites.
5. Complete mineralization of the COCs in the groundwater by indigenous microbes was demonstrated, thereby effecting the complete destruction of these compounds in situ. As densities of contaminant-degraders increased in the groundwater in response to stimulation, the COC concentrations decreased, and the chloride concentrations increased. Complete mineralization of chlorinated solvents results in the production of chloride.
6. The west side of the landfill can be biostimulated with air injection and trace nutrients alone. Immediately after air injection COCs decreased to undetectable levels. The addition of nitrous oxide and triethyl-phosphate may have aided in reducing other compounds present, but was not necessary to effect the bioremediation. In situ respiration tests also showed that this site had a high oxygen demand and thus abundant readily biodegraded compounds. Oxygen was the single most

limiting element for microbes in this part of the landfill. The ability of air injection to alter the dominance of anaerobic processes was further evidenced by the lack of detectable nitrite during times of air injection.

7. The southern side of the landfill can be biostimulated with air, nitrous oxide, triethyl-phosphate and methane. Due to the lower carbon content of the groundwater there are insufficient carbon/energy sources for high bioactivity in this area. Addition of the methane as a co-metabolic carbon/energy source was necessary to obtain reduction of COCs to undetectable levels. This is further evidenced by the in situ respiration test which showed that much higher levels of oxygen saturation were possible at this site and that the environment is normally aerobic or microaerophilic.

8. Biostimulation at both sites remediated both the groundwater and adjacent unsaturated zone of the COCs, but also a large variety of other organic compounds that may become COCs as the landfill ages. Trace amounts of a number of other organic compounds were found at both sites in the groundwater and vadose zone prior to biostimulation. These compounds were reduced to undetectable levels after biostimulation at both sites in both environments. This demonstrates the broad applicability of aerobic in situ biostimulation for remediating organic contaminants at the sanitary landfill and other waste sites at SRS.

Recommendations: The final remediation system should incorporate 2 injection zones along the south and west sides of the landfill. Since groundwater consistently flows parallel to the long axis of the SRS landfill, two horizontal wells, one running along the south side of the southern expansion and the other along the west side, should be sufficient to bioremediate any solvents coming from the site. Based on the optimization test and probable future leaching changes, both injection systems should inject at a depth of 20-30 ft below the water table. This will provide a sparge zone that will biotreat all current and future leachate. Cost analysis will determine if horizontal wells or a series of vertical injection wells are most appropriate. Because of the shallow depth of the wells, the length of the west side, and the need to remediate groundwater associated with the Interim Sanitary Landfill a sequential series of vertical injection wells may be most appropriate for this portion. The remediation system should be able to handle any future leaching from the original landfill, the southern expansion, and the northern expansion since the proposed configuration and prevailing groundwater flow would contain any leachate from these areas. The injection system will consist of a compressor with the ability to add nitrous oxide, triethyl-phosphate, and methane. The south side injection will need to be controlled separately from the west side injection, since different strategies will be necessary for the most cost effective in situ bioremediation. Both wells, however, will need all capabilities as conditions may change as the landfill ages. The results of the Bioremediation Optimization Test have shown that the use of bioremediation via in situ stimulation of indigenous microorganisms is an efficient and cost effective long-term means of obtaining ultimate groundwater restoration at the SRS Sanitary Landfill.

Note: In light of some of the unexpected findings of this study some short term additional studies are recommended. These new studies would determine the most cost effective strategy for operations at the two sites. The questions to be answered would be: 1) what is the minimum interval of injection on and off that would insure bioremediation of both sites, and 2) what is the minimum sampling interval for both areas to insure bioremediation.

5.0 Key Contacts and Participants

Key personnel contacts for each organization are shown below:

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Appendix A VOC Concentrations in Soil Gas.

Site 1 Center Well Gas Sample Data

1TCE-PZ-6D Gas Sample Data

1TCE-PZ-6S Gas Sample Data

1TCE-PZ-7D Gas Sample Data

1TCE-PZ-7S Gas Sample Data

1TCE-PZ-10D Gas Sample Data

1TCE-PZ-10S Gas Sample Data

1TCE-PZ-11D Gas Sample Data

1TCE-PZ-11S Gas Sample Data

1TCE-PZ-13D Gas Sample Data

1TCE-PZ-14D Gas Sample Data

1TCE-PZ-14S Gas Sample Data

2VC-VZP-6D Gas Sample Data

2VC-VZP-6S Gas Sample Data

2VC-VZP-8D Gas Sample Data

2VC-VZP-8S Gas Sample Data

2VC-VZP-9D Gas Sample Data

2VC-VZP-9S Gas Sample Data

2VC-VZP-12D Gas Sample Data

2VC-VZP-12S Gas Sample Data

2VC-VZP-13D Gas Sample Data

2VC-VZP-13S Gas Sample Data

2VC-VZP-14D Gas Sample Data

Site 2 Center Well Gas Sample Data