Hanford Site 100-N Area In Situ Bioremediation of UPR-100-N-17, Deep Petroleum Unplanned Release - 13245

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ABSTRACT

In 1965 and 1966, approximately 303 m³ of Number 2 diesel fuel leaked from a pipeline used to support reactor operations at the Hanford Site's N Reactor. N Reactor was Hanford's longest operating reactor and served as the world's first dual purpose reactor for military and power production needs. The Interim Action Record of Decision for the 100-N Area identified in situ bioremediation as the preferred alternative to remediate the deep vadose zone contaminated by this release. A pilot project supplied oxygen into the vadose zone to stimulate microbial activity in the soil. The project monitored respiration rates as an indicator of active biodegradation. Based on pilot study results, a full-scale system is being constructed and installed to remediate the vadose zone contamination.

INTRODUCTION

Washington Closure Hanford (WCH), under contract to the U.S. Department of Energy, Richland Operations Office (DOE-RL) is currently conducting deactivation, decontamination, decommissioning, and demolition of excess facilities; placing former production reactors in an interim, safe, and stable condition; and remediating waste sites and burial grounds in support of the closure of the Hanford Site River Corridor. The Hanford Site River Corridor consists of approximately 220 mi² along the Columbia River, in Washington State.

The remediation of Hanford Site River Corridor waste sites is authorized using interim action Records of Decision under the CERCLA [1].

BACKGROUND

N Reactor, located in the 100 Area along the Columbia River, was Hanford's longest operating reactor and served as the world's first dual purpose reactor for military and power production needs. Another unique feature of this reactor was that it used petroleum-fired boilers, as opposed to coal, to support reactor operations.

The waste site designated as UPR-100-N-17 is an unplanned petroleum release that occurred at the N Reactor's 166-N Tank Farm sometime between August 1965 and September 1966. Approximately 303 m³ of Number 2 diesel fuel oil leaked from a line between the storage tanks and a day tank. The leak was discovered because of a discrepancy between fuel used and fuel stored. External corrosion of a 0.102-m (10.2-cm) diesel oil supply line caused the line to leak and release diesel oil to the soil. The oil drained through the soil to groundwater where it migrated toward the Columbia River. The line was excavated and repaired in September 1966. During 1967, oil near the river was collected in an interceptor trench and periodically burned off in an attempt to intercept it before it could reach the river.

This unplanned release is one of many releases documented during reactor operations at the 100 N Area and was included in the *Interim Remedial Action Record of Decision for the 100-NR-1/NR-2 Operable Units of the Hanford 100-N Area* [2]. As the preferred remedy for this release, the ROD identified in situ bioremediation of the contaminated soils in the deeper vadose zone (4.6 m below ground surface extending down to the groundwater interface), with bioventing as the selected technology. Bioventing entails supplying oxygen to the unsaturated zone through injection wells and, if necessary, adding bacteria

and nutrients to stimulate existing microbes to biodegrade the petroleum contamination. Monitoring the progress of the bioventing system is planned to be completed through the existing groundwater monitoring well network. Once field screening data indicate that the remedial action goals have been met, a more extensive sampling campaign will be conducted to ensure the remedial action goals identified in the CERLCA ROD are met. The remedial action goal for total petroleum hydrocarbons in the CERCLA ROD for this waste site is based on the *Washington Administrative Code* (WAC) 173-304, "Model Toxics Control Act – Cleanup," [3] cleanup level of 200 mg/kg.

PROCESS DEVELOPMENT

Pilot Project Description

With oversight from the lead regulatory agency, the Washington State Department of Ecology (Ecology), a pilot study was commissioned in 2009 to evaluate the effectiveness of bioventing for remediation of deep vadose zone petroleum contamination.

The scope of the pilot project was to demonstrate remediation of total petroleum hydrocarbon (TPH) contamination in the vadose zone using in situ bioremediation (bioventing) technology. In situ bioremediation consists of adding oxygen to treat deep petroleum-contaminated soils through the use of injection wells constructed at various locations within the contamination zone. The need for nutrient and bacteria addition was also evaluated.

In early 2009, seven bioremediation wells were drilled and constructed at the UPR-100-N-17 site (Fig. 1). Five of the wells were drilled with screened intervals in the deep valoes zone and two were drilled and screened in the shallow valoes zone. Table I shows the well construction details and data for the seven wells.

Groundwater Information

Fluctuations of the Columbia River are regulated immediately upstream of the Hanford Site by the Priest Rapids Dam. River level fluctuations are reflective of a number of cyclical factors including daily, weekly, seasonal, and annual cycles. Daily and weekly cycles are related to hydroelectric energy needs. Seasonal cycles are influenced largely by the spring runoff, along with fish and wildlife management activities. In January and February, in preparation for the spring runoff, the reservoir system is lowered, creating higher river levels. In mid-April, there is another large release of water, which lasts over a month, to facilitate the salmon migration downstream. The largest release of water from the system occurs from May to the end of June, which represents the release of spring runoff [4]. These fluctuations in Columbia River stage influence groundwater elevations in wells located close to the Columbia River. At the UPR-100-N-17 waste site, groundwater elevation fluctuates as much as 3.5 m.

Depth to groundwater encountered during the bioventing well drilling period from January to early March 2009 ranged from 22 to 23 m below ground surface (bgs). These groundwater depth measurements were converted to groundwater elevations using well completion survey data. Since drilling occurred from late January to early March 2009, the 0.7-m differential between groundwater elevations in the bioremediation wells could be actual groundwater table fluctuations caused by short-term (daily or weekly) increases and decreases in river discharge. As described above, drilling of the bioremediation wells was occurring during periods of planned releases at Priest Rapids Dam in order to create storage capacity behind the dam in anticipation of the spring runoff releases.

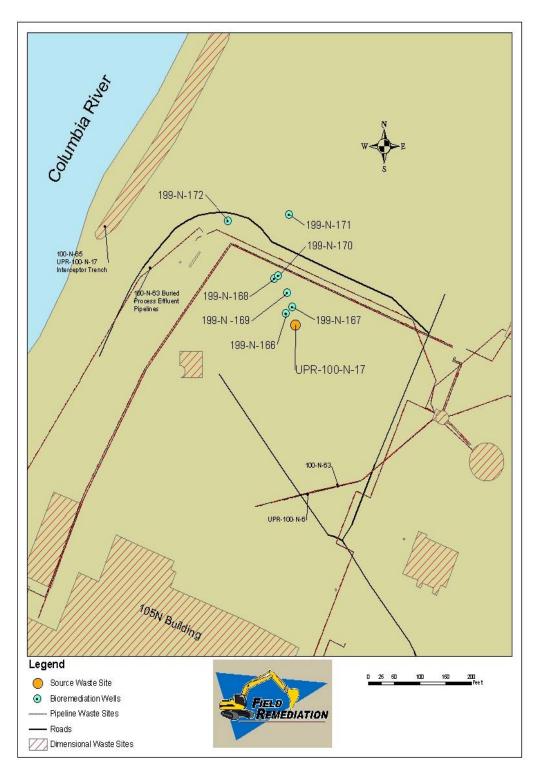


Fig. 1. Location of Bioremediaton Wells in the 100-N Area.

Well Number	Construction Date	Total Depth (ft bgs)	Screen Top (ft bgs)	Bottom of Screen (ft bgs)	Screen Interval (ft)	Well Elevation (ft asl)	Groundwater Elevation ^a (ft asl)	Depth to Water (ft bgs)
199-N-166	01/29/2009	33	10	30	20	461.69	388.53 ^b	73.16
199-N-167	02/09/2009	83	53	78	25	461.33	388.17	73.16
199-N-168	02/25/2009	33	10	30	20	462.02	387.92 ^b	74.10
199-N-169	02/20/2009	83	53	78	25	461.48	387.88	73.60
199-N-170	03/05/2009	83.5	54	79	25	461.66	387.56	74.10
199-N-171	03/13/2009	82.4	55	80	25	462.35	386.85	75.50
199-N-172	01/23/2009	82	57	77	20	461.05	389.15	71.90

Table I. Bioremediaton Well Construction Details

^{a.} Groundwater elevation values represent the construction dates time frame and are not assumed to be static through time.
^{b.} Wells 199-N-166 and 199-N-168 were not completed into the water table. Water elevations are estimated using adjacent deeper well water level measurements.

asl = above sea level

bgs = below ground surface

Seasonal fluctuation of the groundwater table creates a periodically rewetted zone (PRZ) that is coincident with the historic high and low groundwater elevations and results in smearing of petroleum through the PRZ. The PRZ contains the majority of the petroleum contamination at the UPR-100-N-17 waste site and may require additional measures (e.g., bio-sparging) to complete remediation. Remediation of the contamination in the smear zone will be evaluated and addressed in the final CERCLA ROD for the 100-N Area.

Borehole Soil Sampling

The purpose of sampling soils from the borehole during drilling was to support the design and implementation of the bioventing system and to characterize the vadose zone with regards to current physical and chemical conditions and how these conditions might affect bioremediation. Two main goals were met during the drilling and sampling project. Petroleum contamination was located in the vadose zone and soil analysis verified the existence of a microbial population within the vadose zone that was necessary for the bioremediation process to move forward.

Data Requirements

Although much is known about the hydrogeologic conditions of the vadose zone in the 100-N Area, some of the physical and chemical parameters important to successful implementation of bioremediation and bioventing were not available and needed to be collected during well construction and performance of pilot testing. Specifically, data concerning the concentrations of indigenous microbes and nutrients in the subsurface and quantitative site-specific data concerning the nature and extent of petroleum contamination were needed.

Sampling Results

• <u>Microbes:</u> All boreholes were sampled for heterotrophic microorganisms. The purpose was to enumerate the microorganisms in soil samples collected from boreholes at the UPR-100-N-17 site. Heterotrophic microorganisms in the soil include bacteria and fungi that obtain their energy and carbon source for growth and reproduction from organic compounds. This portion of the microbial community can be responsible for degradation of xenobiotic compounds such as diesel. Two

approaches were proposed to be used to enumerate (or estimate) the number of live microorganisms in the soil samples. First was to estimate the total heterotrophic microorganisms using a plate count technique with soil extract agar. The second approach will be based on the outcome of the first approach, and that approach will estimate total diesel-degrading microorganisms using a plate count technique with soil extract agar amended with 10 mg/L diesel No. 2 fuel. A total of 17 soil samples were provided for analysis. These samples ranged in depth with relation to the PRZ, soil moisture, and apparent petroleum odor. All of the soil samples collected at the site exhibited microbial growth. Because of the heavy fungal growth on the initial dilution samples and no growth on plates with the serially diluted samples, the estimate of the soil community is between 100 and 1,000 colony forming units per gram of soil (CFU/g).

• <u>TPH/Oil and Grease:</u> All boreholes were sampled for TPH (diesel and gasoline range) and oil and grease (O&G). TPH and O&G were detected in all boreholes and at levels over the current cleanup level of 200 mg/kg.

The overall trend was to encounter higher concentrations at depths of 16.8 m bgs or greater. Then the contamination was pervasive to groundwater. High concentrations ranging from approximately 3,000 to 4,400 mg/kg were detected in each of the deep boreholes (PRZ).

- <u>Moisture Content:</u> All boreholes were sampled to determine moisture content of the soil. Some general trends of moisture content correlating from borehole to borehole was noted, which suggest some zones within the UPR-100-N-17 site's lithology retain moisture better than other lithologic zones (i.e., silty soil versus sandy soils). Disparity from trends could indicate localized lithologic changes in some boreholes (lenses or stringers of finer grained sediments) or other factors. Moisture contents increased overall as sample depths approached the groundwater table and higher concentrations of TPH were encountered (Fig. 2). The minimum result was 0.2% moisture by weight (mw) and the maximum result was 10% mw. The average moisture content of all samples was 4.59% mw. The 0.2% mw result may be an erroneous result based on surrounding samples' results that have higher result values. The next minimum result was 2.1% mw, and using this value the average moisture content for all samples was 4.63% mw. These average values fall within the range for bioremediation to occur[5].
- <u>Organics:</u> All boreholes were sampled for volatile and semivolatile organic compounds. All sample results were below the current 100-N Area cleanup levels for direct exposure, protection of groundwater, and protection of the Columbia River. This indicates that most or all of the volatile and semivolatile compounds may have volatilized or degraded over time in the UPR-100-N-17 site's vadose zone.
- <u>Nitrogen:</u> The Total Kjeldahl Nitrogen (TKN) method has been reported to be the most reliable method for determining total nitrogen available, which is a valuable nutrient to support microbial growth processes. All boreholes were sampled to determine total nitrogen content in the soil. TKN results detected nitrogen in most of the samples collected. The average TKN concentration of the sample results was 28 mg/kg. This is a relatively low value, but a value that has been reported as adequate to support bioremediation [5].

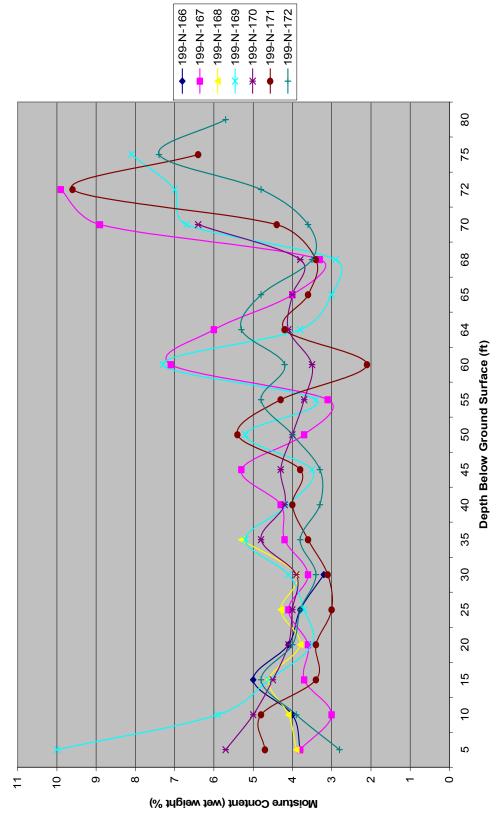


Fig. 2. Chart of Bioremediation Wells Borehole Moisture Content Values at Depth.

- <u>Phosphorus:</u> Phosphorus has been found to be a valuable nutrient that supports microbial growth processes. All boreholes were sampled to determine total phosphorus content in the soil. Phosphorus, as an element, was detected in all samples collected with an average concentration of 543 mg/kg. Phosphorus in this mineralogical form may not be the best available form as a nutrient for the bacteria to metabolize; however, some microbial communities have adapted to uptake phosphorus. Phosphorus in anion form, as a phosphate ion, was analyzed for and the results were nondetected for all boreholes. The phosphate ion is the more bio-available form of the nutrient used by the bacteria. These low concentrations of the phosphate ion in the vadose zone could be a limiting factor for maximum rates of bioremediation to occur during bioventing [6].
- <u>pH:</u> All boreholes were sampled to determine pH content. Results had a range of 6.6 to 9.2 and an average value of 8.6. This average is near the upper range of optimal pH for bioremediation to occur and correlates to previous studies' interpretations of 100-N Area soils as being alkaline.
- <u>Metals:</u> Soil samples were analyzed for RCRA [7] metals as high concentrations may be toxic to bacterial processes. Metal toxicity to microorganisms is a complex subject and beyond the scope of this report. Generally, the presence of metals has very little direct effect on the bioremediation process as the microbial population frequently adapts to the concentrations present. The sample results will be used as a baseline and for future reference if problems occur with the bioventing process and metal toxicity needs to be investigated as a limiting factor.
- <u>Radionuclides:</u> These analyses were necessary to characterize the vadose zone for radiological hazards that might cause worker safety issues or affect the presence of microbial activity in the soil. Radionuclides have been detected in the groundwater at the 100-N Area, historically, due to reactor processes that occurred during operations. Well 199-N-172 was the first well drilled and constructed. A full range of radionuclides were analyzed using gamma spectrum analysis. All results were for nondetected; therefore, further borehole soil samples were analyzed for total beta radiostrontium only, as strontium-90 is a known groundwater contaminant at the 100-N Area. All samples collected had results below the cleanup level of 4.5 picocuries per grams (pCi/g) for total beta radiostrontium. The highest sample result was 1.8 pCi/g and was taken from well 199-N-171. Geophysical logs were run to detect the presence of man-made and naturally-occurring radionuclides in the soil.

The sample result data were helpful in constructing an initial conceptual model for the UPR-100-N-17 site. Microbial sample results show that there were colonies of bacteria and other microorganisms living in the vadose zone; therefore, bioventing pilot testing was expected to be successful to some degree.

PILOT TEST OPERATIONS

Equipment and facilities required for all phases of the pilot testing included seven bioremediation wells; a 20-horsepower regenerative blower (Fig. 3); a flow-control manifold (Fig. 4); ancillary hoses, valves, and fittings; and electrical supply and controls for the blower.

The electrical controls, flow-control manifold, and blower are housed in a transportable steel container (skid). The bioremediation wells were connected to the manifold using flexible hoses and quick-disconnect couplers. Initially, power was provided by a portable diesel generator. Following the respirometry test program, a fixed power line was routed to the bioventing skid and used for the remainder of the test program.



Fig. 3. Blower Package inside Container.



Fig. 4. Air Distribution Manifold.

Respirometry Test

The in situ respiration test was initiated in February 2010. The objective of this test was to determine an oxygen-utilization rate and associated microbial-respiration efficiency in the zone surrounding each well. The subsurface was thoroughly aerated by blowing atmospheric air into each of the seven test wells.

After aerating the subsurface for a period of 41 hours, the blower was shut off and the oxygen and carbon dioxide levels in each well were measured over time. The rate of oxygen decrease is related to the level of microbial activity (respiration) in the subsurface as organic matter is consumed. The rate of oxygen depletion was calculated and used to evaluate the effectiveness of bioremediation as a means of degrading the petroleum hydrocarbon contamination. Aerating the subsurface for a period of approximately 48 hours prior to these measurements mitigates the potential for oxygen decreases due to concentration gradient-induced diffusion.

Prior to the respiration test startup, initial baseline soil gas monitoring was conducted in January 2010. After purging each well casing, soil-gas samples were collected from the seven bioremediation wells and analyzed for oxygen, carbon dioxide, methane, and total volatile hydrocarbons (TVH). Each sample was collected into a Tedlar® bag and then analyzed using direct-read field instruments. Table II shows the baseline concentrations for each of these parameters.

Monitoring Point	Baseline Oxygen (%)	Baseline CO ₂ (%)	Baseline TVH (ppmv)	Baseline Methane (%)
DIW-1 (199-N-166)	4.1	13.3	60.63	0.2
DMP-1 (199-N-169)	1.6	14.9	3.93	0.0
DMP-2 (199-N-170)	1.5	14.9	92.34	0.2
DMP-3 (199-N-171)	2.3	13.8	109	0.2
DMP-4 (199-N-174)	1.3	15.6	16.34	0.0
SIW-1 (199-N-166)	20.2	1.3	84.32	0.1
SMP-1 (199-N-168)	20.3	0.8	117	0.2

Table II. Baseline Concentrations in Bioremediation Wells

DIW = deep injection well

DMP = deep monitoring point

ppmv = parts per million by volume

SIW = shallow injection well

SMP = shallow monitoring point

TVH = total volatile hydrocarbons

Aeration of the subsurface was performed by connecting the bioremediation wells to the blower manifold and operating the blower for a period of 2 days. Valves on the control manifold were used to regulate the air flow to each well at approximately 0.42 m³/min. Samples were collected on a predetermined schedule starting on February 26, 2010, immediately following shutoff of the blower, and continuing through test completion on March 10, 2010. In total, 27 samples were collected from each of the bioremediation wells over a period of approximately 292 hours (12 days).

Air Injection Radius of Influence Testing

Air injection testing was conducted to evaluate the radius of influence (ROI) of the test wells. ROI is a critical design parameter for bioventing applications, as it helps establish the number of injection wells needed and the spacing between wells. For the purposes of this pilot test, two air-injection tests were completed – a deep injection test and a shallow injection test. For each test, air was injected into one bioremediation well and the soil gas in the remaining six wells was monitored for pressure, oxygen, carbon dioxide, methane, and TVH over time.

The deep-injection ROI test was conducted in September 2010, whereby air was continuously injected into well DIW-1 at a flow rate of 9.9 m3/min. Soil/gas monitoring at the other bioremediation wells was performed throughout the injection period, starting with baseline sampling on September 20, 2010, and continuing through test completion on September 27, 2010. Thirteen rounds of measurements for pressure, carbon dioxide, oxygen, methane, and TVH were made at each of the six monitoring points over a period of approximately 165 hours (about 7 days).

The second (shallow) injection ROI test was conducted in October 2010, similar to the deep injection test except air was injected into well SIW-1 at a flow rate of 9.9 m3/min. The other six bioremediation wells were monitored on a predetermined schedule beginning on October 4, 2010. The shallow test was terminated on October 18, 2010. Eighteen rounds of vapor measurements were made at each of the six monitoring points over a period of approximately 334 hours (about 14 days).

Six-Month, Long-Term Operation Test

The 6-month, long-term operation test was completed to verify that elevated oxygen concentrations can be sustained in the deep vadose zone, and to evaluate the mechanical reliability of the blower and associated equipment. This test was intended to verify the suitability of the selected blower package and identify long-term operations and maintenance needs of the system, including operations during both warm and cold weather conditions.

The 6-month, long-term operation test was initiated on October 18, 2010, when the shallow well ROI pilot test was completed and baseline samples for the 6-month, long-term operation test were collected. The bioventing system was operational from October 21, 2010, to May 14, 2011. The 6-month, long-term operation test concluded on May 18, 2011, when the final monitoring event was conducted. Throughout the testing, air was injected into DIW-1 and DMP-4 at a rate of 7.1 m³/min per well. A Bioremediation Well Location Map is provided as Fig. 1. A sampling event was conducted 2 weeks after system startup (2-week monitoring event) to determine if the injection rates and locations were adequate to enhance oxygen concentrations throughout the pilot study deep injection zone. The injection rates and locations were adequately selected for the purposes of the 6-month, long-term operation test and no changes were made to the testing program. Monitoring was then conducted monthly for the duration of the test.

Three deep monitoring wells (DMP-1, DMP-2, and DMP-3) were used to evaluate changes in the soil/gas composition. The wells were monitored for oxygen, carbon dioxide, methane, TVH using a Mini-Rae 4-gas meter[™], and pressure at the wellhead. The shallow bioremediation wells were not monitored during the 6-month, long-term operation test because oxygen concentrations in these wells have been consistently near oxygen saturation throughout the previous pilot study testing.

PILOT TEST RESULTS

Results of the study indicate that air injection alone is sufficient to stimulate microbial activity in the deeper vadose zone and the radius of influence is sufficient to encompass the entire contamination plume.

Respirometry Testing

An in situ respiration test was conducted in February and March 2010 to determine the feasibility of bioventing. Biodegradation efficiency is related to the oxygen-utilization rate and is calculated using Eq. 1.

$$K_b = \frac{-k_o \,\theta_a \,\rho_{o2} \,C \times 0.01}{\rho_k} \tag{Eq. 1}$$

where (calculated or assumed values for the site follow each description):

 K^{b} = biodegradation rate calculated in mg hydrocarbon consumed per kg of soil per day

- k^{o} = oxygen utilization rate calculated for each monitoring point in %O2 consumed per day
- θ^a = gas-filled pore space (volumetric content at the vapor phase) = 0.27 cm3 gas/cm3 soil
- ρ^{O2} = density of oxygen; assumed soil temp of 50 °F = 1,378 mg/L [8]
- C = mass ratio of hydrocarbons to oxygen required for mineralization (calculated assuming diesel as C10H20 and stoichiometric relationship of C10H20+ 15O2 => 10CO2 + 10H2O) = 0.29
- ρ^{k} = soil bulk density; assumed value from assumed site soil characterized as mixed grain sand, dense = 1.86 g/cm3 [8]
- θ : = total porosity (where $\theta = 1 \rho k/\rho T$) = 0.30 cm3/cm3
- θ^{w} = water filled porosity (where $\theta w = M*\rho k/\rho T$) = 0.03 cm3/cm3

 ρ^{T} = soil mineral density; assumed value = 2.65 g/cm3

M = moisture content; 4.63% reported site average [9] = 0.0463 g moisture per g soil.

Baseline measurements of oxygen and carbon dioxide and subsequent calculated biodegradation rates are presented in Tables III and IV. During the respiration test methane was detected infrequently at 0.1%. The highest levels of TVH, up to 130 ppmv, were detected on the first day of sampling. TVH levels generally decreased over the duration of the test.

In general, oxygen utilization rates of 1% per day or greater indicate treatment by bioventing to enhance microbial activity is feasible. Lower oxygen utilization rates in areas with significant hydrocarbon content indicate that other factors may be limiting biodegradation such as insufficient nutrients or moisture, low temperature, or contaminant toxicity. Results from wells DIW-1, DMP-1, and DMP-2 indicate remediation by bioventing is feasible. Results from the shallow wells (SIW-1 and SMP-1) indicate either a lack of significant hydrocarbon mass, inhibition of biodegradation, or that these locations have significant air exchange with the atmosphere, such that oxygen depletion is not occurring due to respiration.

The results from DMP-3 and DMP-4 indicate that biodegradation of hydrocarbons is occurring; however, the relatively low oxygen utilization rate indicates a lower efficiency compared to the other areas. It is possible that the environment in the vicinity of these wells is limiting microbial activity due to some other factor such as moisture or nutrient deficiency. Another possibility is that the initial population of microbes capable of aerobically degrading the hydrocarbons was lower in these areas, and so there was a lower apparent response time to the introduction of oxygen.

Monitoring Point	Baseline O ₂ (%)	Baseline CO ₂ (%)	O ₂ after 41-hr aeration (%)	CO ₂ after 41-hr aeration (%)
Deep Injection Well -1	4.1	13.3	20.8	0.0
Deep Monitoring Point -1	1.6	14.9	20.8	0.1
Deep Monitoring Point -2	1.5	14.9	21.0	0.0
Deep Monitoring Point -3	2.3	13.8	21.1	0.0
Deep Monitoring Point -4	1.3	15.6	21.1	0.1
Shallow Injection Well -1	20.2	1.3	21.0	0.1
Shallow Monitoring Plan -1	20.3	0.8	21.0	0.0

Table III. Respirometry Test – Initial Bioremediation Well Measurements

Monitoring Point	O2 Utilization (%/day)	Biodegradation Rate (mg/kg-day)
Deep Injection Well-1	1.32	-0.76
Deep Monitoring Point-1	1.29	-0.74
Deep Monitoring Point -2	0.96	-0.55
Deep Monitoring Point -3	0.49	-0.28
Deep Monitoring Point -4	0.71	-0.41
Shallow Injection Well-1	0.20	-0.11
Shallow Monitoring Plan-1	0.18	-0.11

In this analysis, several of the parameter values used to calculate the degradation rate were estimated. For example, a simple sensitivity analysis of soil bulk density over the range of probable values had an impact of up to 64% difference from the initially calculated rate. Therefore, determination of an appropriate bulk density is important in biodegradation rate calculations. Bulk density data from a recently drilled well in the vicinity of the bioremediation well network is being used to help refine the biodegradation rate.

Radius of Influence Testing

A deep injection ROI test was completed in September 2010. Air was continuously injected into DIW-1 at a rate of 9.9 m³/min. All of the six monitoring points exhibited an increase in oxygen concentrations and a decrease in carbon dioxide concentrations as a result of the air injection at DIW-1. Well DMP-4 is the farthest well from DIW-1 at approximately 61 m away. Measurable changes in oxygen and carbon dioxide were observed in DMP-4 within 50 hours of injection. The testing indicates that an effective ROI for DIW-1 is at least 61 m under the testing conditions.

It is important to note that ROI calculations are a function of several parameters, and that the test conditions should be stated for any ROI claim. For the testing described herein, the deep well ROI of 61 m was obtained at an airflow of 9.9 m³/min into a bioremediation well with a 7.6 m screen installed from 16 to 24 m in a sandy, relatively dry and homogenous environment. The stated ROI may or may not be reproducible at other sites with different test conditions. It should also be noted that the ROI was based primarily on the observed change in soil gas composition (oxygen increase) at distant monitoring points, not on an observed subsurface pressure gradient. While pressure differences were noted in monitoring

points relatively close to the injection location, measurable changes in pressure decrease rapidly as the distance from the injection well increases. Changes in soil/gas composition are a more reliable measure of bioventing influence at distant monitoring points.

A shallow injection ROI test was conducted in October 2010 using SIW-1 as the injection well. Results indicate that the shallow air injections did not have an appreciable effect on shallow or deep subsurface conditions and are not likely to significantly enhance microbial activity. In general, the oxygen and carbon dioxide concentrations hovered near the baseline conditions observed in each well prior to starting the shallow ROI injection test, even after more than 300 hours of air injection. Because the baseline oxygen concentration is near atmospheric levels in the shallow wells, oxygen is not a rate-limiting factor for biodegradation in shallow soils.

Six-Month, Long-Term Operation Test

The 6-month, long-term operation test was conducted between October 2010 and May 2011. DMP-1, DMP-2, and DMP-3 exhibited oxygen concentrations that increased significantly over the baseline conditions and were near oxygen saturation throughout the pilot study. Carbon dioxide concentrations also dropped significantly in these wells. Each well exhibited a measurable increase in pressure, indicating air flow from DIW-1 and DMP-4 was adequate to influence the entire study area. In DMP-2 and DMP-3 the TVH concentrations measured at the wellhead peaked at around day 100 (2,400 hours) of the test and then declined. All three deep monitoring points exhibited a small peak in TVH near the end of the testing at around day 187 (4,500 hours). Methane was detected only one time; the detected methane concentration was 0.1% in well DMP-2 during the baseline monitoring.

Of note is the final monitoring event, which was conducted after the bioventing system was shut down. The system shut down due to a power failure on May 14, 2011, after approximately 205 days (4,920 hours) of operation. This shutdown coincided with the conclusion of the 6-month, long-term operation test and the system was not restarted. The final monitoring event was conducted on May 18, 2011, approximately 4 days after system shutdown. The final monitoring event shows a slight decrease in oxygen concentrations and a corresponding rise in carbon dioxide concentrations. TVH concentrations also dropped significantly. Although it is difficult to assess the effectiveness of the pilot system without collecting soil samples, these observations indicate that oxygen and hydrocarbons are being consumed to produce carbon dioxide; therefore, long-term bioventing is likely to be effective at enhancing microbial degradation of deep vadose zone hydrocarbons.

Pilot Test Conclusion

Results of the study indicate that air injection alone is sufficient to stimulate microbial activity in the deeper vadose zone and the radius of influence should be sufficient to encompass the entire contamination plume.

Bioventing appears to be an effective and efficient method of promoting in situ bioremediation in the deep vadose soils at this site. The well spacing and flow rates used during the 6-month, long-term operation test are capable of significantly increasing and sustaining deep vadose zone oxygen concentrations over a large area. The two 6-month test injection wells, DIW-1 and DMP-4, are approximately 61 m apart and the zone between them reached near atmospheric levels of oxygen shortly after the air injection was initiated (7.1 m³/min each). This suggests that the effective radius of influence of these deep wells was at least 61 m.

The 6-month, long-term operation test demonstrates the suitability and reliability of the equipment used provides useful information for full-scale expansion of the technology. The results of the 6-month, long-

term operation test provide strong support for continued bioventing to reduce hydrocarbon concentrations in the deep vadose zone.

The following conclusions can be made from the pilot test results:

- Overall microbial degradation of hydrocarbons is significantly enhanced through bioventing in the vadose zone of this test area. Some variation in oxygen utilization rates were noted between monitoring wells. Factors besides the presence of oxygen that may be affecting the efficiency of degradation in some areas include soil moisture, nutrient availability, and/or contaminant mass presence.
- The equation used to calculate degradation rate is sensitive to assumptions made about physical soil parameters such as bulk density. Future bioventing tests should include the collection of soil samples for contaminant analyses, geotechnical parameter testing, nutrients, and moisture evaluation.
- The ROI for DIW-1 is at least 61 m under the specific test conditions employed. Similar ROIs are expected for the other deep bioremediation wells, since the lithology at depth is relatively homogenous across the test area.
- Microbial degradation in the shallow wells (SIW-1 and SMP-1) is not measureable using the protocols established for this testing. Baseline soil vapor levels for oxygen and carbon dioxide are at atmospheric concentrations. Oxygen is not rate limiting with respect to bioremediation in the shallow vadose zone. Bioventing in the shallow soils of this test area will have a negligible effect on microbial degradation rates.
- Bioventing appears to be an effective and efficient method of promoting in situ bioremediation in the deep soils at this site. Depressed baseline oxygen levels are clearly a key rate-limiting factor. Even at moderate air flow rates, bioventing has been shown to affect a large area around injection wells, suggesting the soils are relatively permeable to air flow.
- After 2 weeks of injection, it appeared that two injection wells (DIW-1 and DMP-4) were adequate to significantly increase deep vadose zone oxygen concentrations throughout the entire pilot study area when operated at a flow rate of 7.1 m³/min each.
- Soil vapor samples collected after 4 days of system shutdown showed a clear decrease in subsurface oxygen levels that can be assumed to indicate that microbial degradation continues at measurable rates.

REMEDIATION PROCESS IMPLEMENTATION

Design

Based on the results from the pilot study, and with concurrence from Ecology, a full scale bioventing system has been installed to begin remediation of the contaminated soil in the deep zone of this waste site. A skid similar to the one used in the pilot study currently is injecting atmospheric air into two of the deep wells (DIW-1 and DMP-4). The system utilizes three redundant 7.5 hp blowers to supply 7.1-8.5 m³/min air to the deep zone to stimulate existing microbes to enhance microbial biodegradation.

Problems Needing Resolution

The CERCLA ROD for this waste site requires the addition of bacteria and nutrients to enhance microbial biodegradation, if needed to ensure successful bioremediation. Further data is needed to determine whether the addition of bacteria and nutrients will enhance microbial biodegradation. Archived soil samples taken during installation of the bioventing wells, in addition to contaminated soil from nearby excavations, will be further analyzed to determine whether the existing microbes are of the type and of sufficient quantity to ensure successful microbial biodegradation. This analysis will also evaluate whether the addition of nutrients and bacteria will enhance microbial biodegradation and provide information on the amount of nutrients or bacteria that could be supplied to ensure optimum utilization by existing bacteria colonies (ensure amount supplied, if needed, are not toxic or outcompete the existing colonies). In addition, confirmation that the ROI is adequate to encompass the entire contaminated plume is needed. Data obtained during operation of the bioventing system will evaluate if the ROI of the system is sufficient to treat the entire plume of contamination.

Path Forward

Ecology has approved plans to procure and install the final bioremediation system in 2012, utilizing the existing injection and monitoring wells constructed to support the pilot study. WCH continues to install the system and prepare a performance monitoring plan that will evaluate effectiveness of the system in reducing contaminant concentrations in soil, determine whether the addition of nutrients and bacteria is required to meet milestone requirements, and document the method for ensuring that remediation of the site has met the cleanup goals. Successful remediation of the petroleum contamination will take numerous years to accomplish; however, this project will demonstrate how deep vadose zone petroleum contamination can be cost effectively treated by using bioventing and will help determine whether the addition of nutrients and bacteria are beneficial in enhancing the rate of microbial biodegradation.

CONCLUSION

Results of the pilot study indicate that air injection alone is sufficient to stimulate microbial activity in the deeper vadose zone and the radius of influence is sufficient to encompass the entire contamination plume. Installation of the full scale system was accomplished in December 2012 and a performance monitoring plan is in development that will monitor the effectiveness of the system and evaluate when it is believed that bioremediation has met the CERCLA [1] cleanup goals. The performance monitoring plan will also detail activities necessary to ensure, through sampling, that cleanup goals have been met and remediation of the site is complete.

REFERENCES

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- 5 EPA, Principles and Practices of Bioventing Manual, Volume I: Bioventing Principles EPA/540/R-95/534a, U.S. Environmental Protection Agency, Office of Research and Development National Risk Management Research Laboratory Center for Environmental Research Information, Cincinnati, Ohio (1995).
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