INTERMEDIATE-SCALE EVALUATION OF BIOREMEDIATION TECHNOLOGIES IN HETEROGENEOUS LNAPL-CONTAMINATED SOIL

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ABSTRACT

Bioremediation is a potentially cost-effective, *in situ* method for cleaning up NAPL-contaminated sites. The ability of microorganisms to access and degrade NAPL constituents is highly dependent on the heterogeneity of the soil and the morphology of the NAPL source. Soil heterogeneities can result in preferential pathways of air and water flow through the subsurface. Intermediate-scale studies were conducted to evaluate two bioremediation alternatives for a railyard contaminated with aged diesel. Bioventing and biosparging technologies are based on the ability to introduce oxygen to the contaminated zone. Intermediate-scale tests were conducted with aged diesel oil and soil obtained from the site to determine the ability of these technologies to deliver oxygen into a smear zone containing free-phase LNAPL. Results indicate the presence of soil heterogeneities and free-phase NAPL significantly reduce the efficiency of oxygen delivery. Both technologies can increase the overall dissolved-oxygen (DO) concentration in groundwater. However, the airflow occurs primarily through preferential pathways. The result is a lower oxygen delivery than expected, based on bulk-phase DO measurements.

Key words: *NAPL, bioremediation, heterogeneous, intermediate scale*

INTRODUCTION

Bioventing is an application of soil vapor extraction by which air is introduced into the contaminated zone to stimulate aerobic biodegradation. Bioventing can involve the pumping of vapor out of the vadose zone, or the pumping of water from the saturated zone, to induce a significant drawdown of the water table. The resulting introduction of air to previously anaerobic zones can potentially induce more rapid degradation of target compounds. At the test site, in the presence of LNAPL and a fluctuating water table, the contaminant is characterized by a smear zone of LNAPL when water tables are depressed. The potential application of bioventing, therefore, would involve the drawdown of the water table to the bottom of the smear zone to introduce air. Biosparging is the process of injecting air into the saturated zone to deliver oxygen to the contaminated zone and enhance biological degradation of diesel oil. Depending on the soil type, direct injection of air can result in preferential pathways of air flow. These preferential pathways will result in reduced oxygen delivery to the bulk of the soil (Sutherson, 1997).

In intermediate-scale tests, the unsaturated zone is effectively aerobic due to the tank scale. This is a critical difference between intermediate and field studies. The result is that introduction of pumped air into the vadose zone or dewatered smear zone did not change the gas-phase oxygen concentration. Intermediate-scale tests were therefore conducted to measure the oxygen delivered into the saturated phase under a pulsed bioventing/dewatering remedial scheme. Because gas-phase oxygen concentrations remained constant (at approximately 21%) in the unsaturated and dewatered smear zones, the effectiveness of this remedial system at the intermediate scale was assessed by the ability to deliver oxygen to the saturated zone upon reestablishment of the water table. This was accomplished through measurements of dissolved oxygen after individual pulses of water drawdown. Passive drawdown via gravel wells at either side of the intermediate tanks can be viewed as a surrogate for a pump system for groundwater drawdown.

The purpose of the intermediate-scale tests was to assess the efficacy of using bioventing with pulsed pumping or biosparging to meet acceptable endpoints at a diesel-contaminated site. An additional purpose was to illustrate the impact of geologic characteristics of the contaminated site, in particular soil heterogeneity, on homogenous soil dewatering and oxygen delivery.

BACKGROUND

In most natural systems, aerobic biodegradation of biodegradable compounds in the saturated zone and in some unsaturated zones is rate limited by the availability of oxygen. Bioventing and biosparging represent technologies designed to introduce air into the zone of contamination. Although alternative chemical species can be utilized by degrading microorganisms (e.g. iron, manganese, sulfate, nitrate), the energy derived from these species is typically less than that acquired from oxygen. The result is that microbial communities that utilize oxygen can metabolize the target compound faster and replicate faster, resulting in decreased degradation times.

Aerobic biodegradation of petroleum products has been well documented (Parker and Burgos, 1999; Moller et al., 1996; Stout and Lundergard, 1998; Widrig and Manning, 1995). In general, lower molecular weight compounds are biodegraded faster than higher molecular weight compounds (Parker and Burgos, 1999). Degradation rates of fresh diesel is on the order of 5 mg diesel/kg soil/day in batch studies with unlimited oxygen present (Parker and Burgos, 1999). This value was highly dependent on the nature of the soil. Soil columns amended with nutrients showed degradation rates of approximately 14 mg TPH/kg soil/day (Widrig and Manning, 1995). The same study showed a decreased degradation rate when oxygen was not continuously present. At the mesocosm scale (6m^3 of soil), oxygen amendments resulted in degradation rates of approximately 23 mg diesel/kg soil/day (Moller et al., 1996).

Several conclusions are possible based on these previous studies. There appears to be a trend toward increasing degradation rates from batch to larger scales. However, this trend is based on a comparison of studies under different soil, oxygen, and nutrient amendments. Therefore, any conclusion based on these trends must be verified under the specific soil, groundwater, and oxygen parameters available at the site of interest.

Several factors are important in the design and implementation of an *in situ* air introduction system: determination of a contaminant-degrading microbial population, maintenance of oxygen levels to match aerobic degradation rates, maintenance of soil moisture content, and addition of nutrients (Suthersan, 1997; Moller et al., 1996). Based on batch studies, a diesel-degrading microbial culture is present at the contaminated railyard. In a dewatering scheme, such as the method tested during bioventing, and in a soil system with large water retention, the maintenance of soil moisture content is also not a significant concern. Nutrient amendment issues were not tested in this work. Intermediate scale tanks were therefore constructed to test for the ability of bioventing and biosparging to deliver oxygen to the diesel smear zone.

Oxygen delivery is dependent on the water retention and heterogeneity of the soil. Soils with large water retention will tend to have poor de-watering. Therefore, when the water table is depressed from pumping, the amount of air that is able to permeate into the smear zone will be limited. Heterogeneities in the soil, including zones of different permeabilities and the presence of LNAPL pools trapped in the soil matrix, will tend to cause heterogeneities and preferential pathways of air distribution. The result is regions of the soil matrix that will be well aerated contiguous to regions that remain relatively anaerobic. These anaerobic regions will experience some increase in oxygen concentration due to diffusion from aerated zones. However, the extent of oxygen increase is dependent on several factors including volume, contact area, and permeability to gas.

Due to the complexity involved in measurements of biological activity and oxygen delivery, experiments were conducted in well-controlled, intermediate-scale soil tanks. This experimental design allowed the detailed spatial and analytical measurements required for characterization of the effects of heterogeneity on bioventing and biosparging processes.

MATERIALS AND METHODS

Tank construction

A two-dimensional, intermediate-scale soil tank was constructed to perform the experimental investigation of bioventing and biosparging technologies. The tank was made with a 0.5-in.-thick aluminum base and 0.5-in.-thick Plexiglas walls and endplates. Tank dimensions were 8 ft long x 4 ft high x 0.25 ft wide. Six hundred side wall ports, located on a 2-in. uniform square grid, were installed throughout for the purpose of high-resolution fluid sampling. Perforated piping (0.75 in.) was placed at the bottom of the tank to pump or release water from soil. The pipe was connected to a constant head tank supply to control water table elevation inside the tank. Such a system was necessary for accurate control of experimental water level fluctuations.

Tank packing

Desiccated site soil (shipped to Colorado School of Mines and air dried over two months by tilling) was packed within the soil tank. An incremental packing technique was used to produce bulk soil properties whereby the range

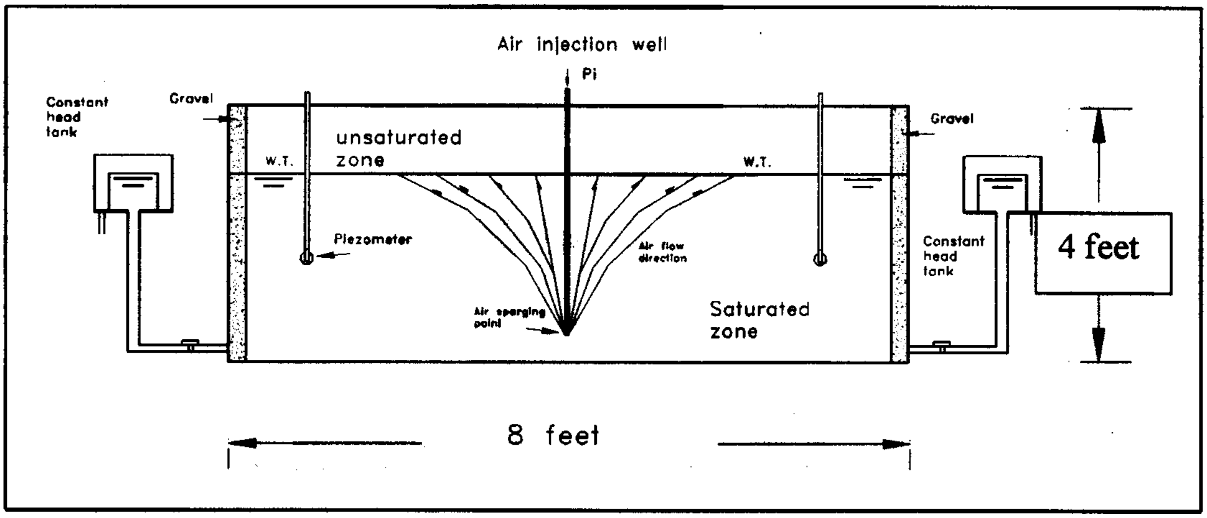

Figure 1. Diagram of intermediate-scale tank for bioventing/biosparging processes. Diagram shows only two of the six monitoring wells/piezometers and illustrates the air flow from the aspirator in biosparging tests.

of particle sizes was distributed homogeneously (that is, no gross layering of the soil was produced). Such an arrangement was deemed representative of the overall spatial distribution of natural heterogeneity in the subsurface at the site. To prepare the tank in this fashion, the coarse fraction of the soil (pebbles and cobbles up to 2.5 in. diameter of long grain axis) was first separated from the bulk soil with a large, 0.5-in. sieve. Next, the separated fractions of fine and coarse soil were alternately layered in the tank to produce a closest packing arrangement. The fine soil was induced (through physical mixing/packing) to sift down into the coarse layer below. The packing process was repeated until the tank was filled with dry soil to within 6 in. of the top. An aspirator (for biosparging) and six observation wells were placed in the tank during packing. Gravel wells at either end of the tank served as surrogate drawdown wells for bioventing processes. A schematic diagram of the bioventing/biosparging tank is shown in Figure 1.

Aspirator tests

An aspirator was placed in the tank to a depth of five feet. A diagram of the aspirator tip construction with air flow is shown in Figure 2. Before soil packing, the aspirator was tested for flow rates and dispersal in water. The aspirator was tested by connection to an air pump with inlet flow varied between 700-1500 acfm (based on typical values for airflow in bioventing processes (Suthersan, 1997).

Bioventing processes

The tank was filled to within six inches of the soil surface with degassed water (dissolved oxygen of approximately 1 mg/L to match reported site groundwater conditions). Prior to each bioventing event, the dissolved oxygen at several points in the tank was measured by syringe sampling. Bioventing events consisted of lowering the water table by two feet using the constant head system shown in Figure 1. The water table was allowed to stay at the depressed level for one hour. The water table was

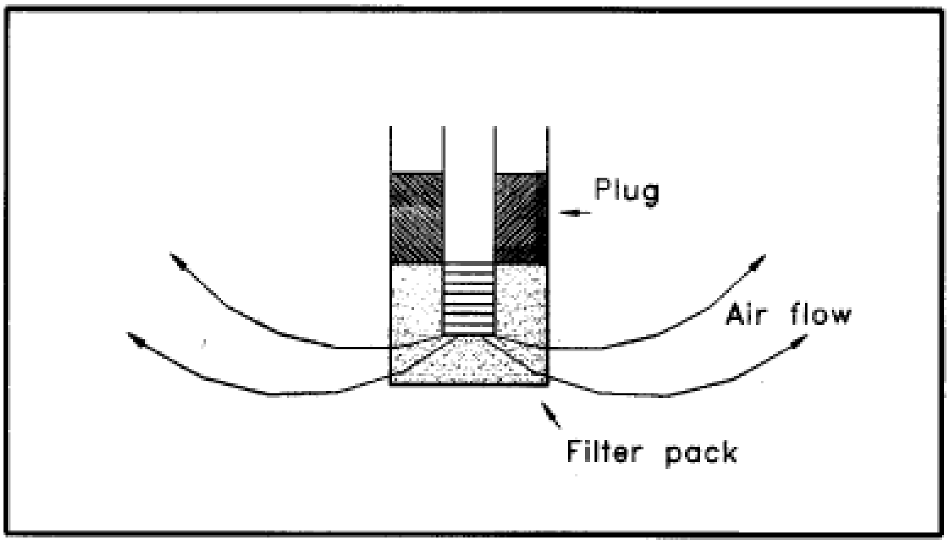

Figure 2. Diagram of aspirator tip.

then raised and dissolved oxygen was measured immediately by syringe sampling from the same sampling ports used in pre-venting measurements. After each venting, the water level was allowed to remain static over the course of one to two weeks during which dissolved oxygen was periodically sampled. Sampling of static water columns was performed to determine oxygen depletion rates for comparison to bench-scale studies. Four bioventing events were conducted: two without oil present and two after oil spill. This experimental approach was designed to test for differences in oxygen delivery from the presence of free-phase LNAPL.

Biosparging processes

The tank was filled to within six inches of the soil surface with degassed water (dissolved oxygen of approximately 1 mg/L to match reported site groundwater conditions). Prior to each biosparging event, the dissolved oxygen at several points in the tank was measured by syringe sampling. Biosparging events consisted of injecting air via air pump into the aspirator well. After each sparging event, dissolved oxygen was measured immediately by syringe sampling from the same sampling ports used in pre-sparging measurements. After each sparging, the tank was allowed to remain static over the course of one to two weeks during which dissolved oxygen was periodically sampled. Sampling of static water columns was performed to determine oxygen depletion rates for comparison to bench-scale studies. Water level was also measured before, during, and after sparging events using the six piezometers installed in the tank. Three biosparging events were conducted: two without oil present and one after the oil spill.

Oil spill procedures

The water table was raised until it was six inches from the tank top. Thirteen hundred ml of diesel oil collected at the site was spilled over a distance of three feet around the sparging well placed in the middle of the tank. Following the LNAPL surface spill, water level in the tank was

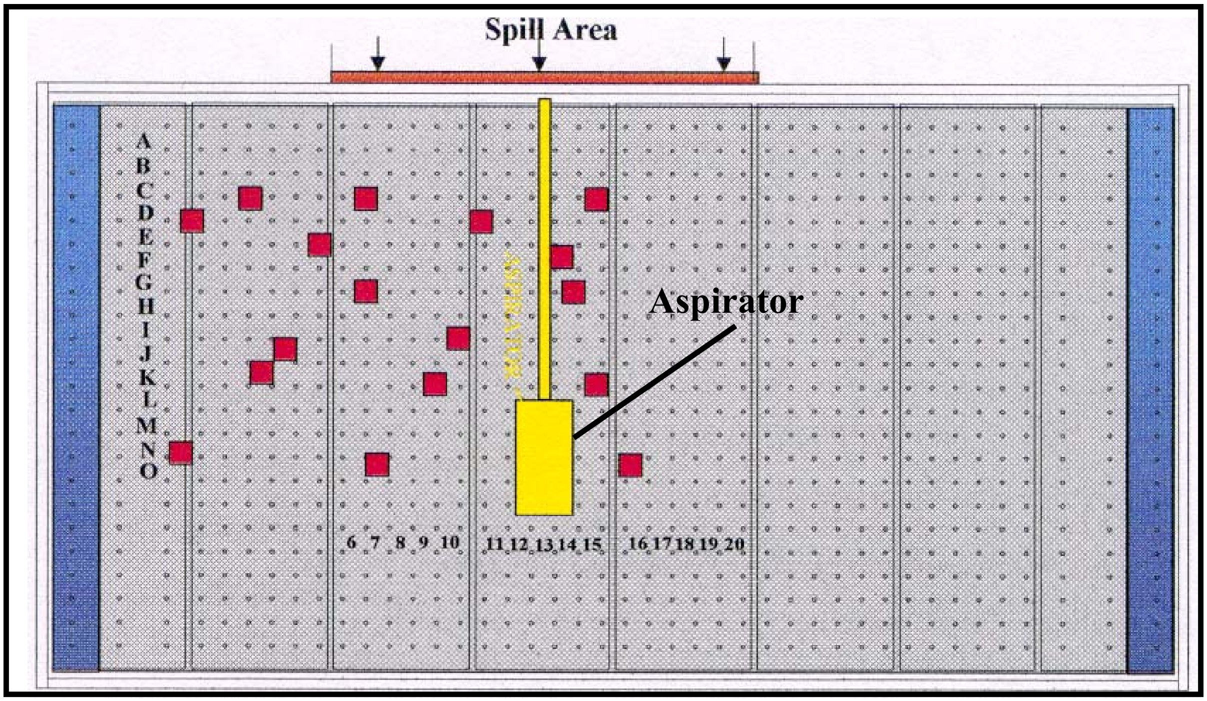

Figure 3. Location of sampled ports in bioventing and biosparging dissolved-oxygen measurements. Squares represent sampling points. Height is not to scale.

fluctuated up and down over a 2.5 ft spill region to simulate seasonal water table fluctuations and to produce a diesel smear zone close to the water table.

Dissolved oxygen sampling

Dissolved oxygen measurements were accomplished using a Hach portable Sension 6 dissolved-oxygen and temperature probe calibrated to water-saturated air using appropriate corrections for salinity and altitude. Samples were pulled from the tank through septa-lined ports using 20-ml syringes. The samples were then placed into a 30-ml glass vial with threaded edge and magnetic stir bar. The DO probe was fitted with a vial cap and Teflon septa to prevent gas exchange during measurement. Measurements were taken during constant stirring. The presence of free-phase diesel and/or diesel sheen was also noted.

Sampling ports were selected to provide a vertical and horizontal cross section of the tank. This cross section allowed assessment of the spatial distribution of air infiltration, as well as determination of the variability in air permeability due to soil heterogeneities and variations in dewatering. A diagram of the tank showing sample port locations is given in Figure 3. Figure 3 also illustrates the port designation nomenclature. Ports are numbered horizontally from left to right and assigned letters from A to N vertically (A at the surface, N at 2.5-foot depth). Samples were also selected to measure DO inside and outside of the spill zone (6-20), and above and below the low water mark for bioventing events (N/O). The high water table mark is at B/C.

RESULTS

Bioventing

The change in dissolved oxygen after a bioventing event (a single drawdown and restoration of the water table) was measured before the diesel oil was spilled onto the tank. The average results of the two bioventing tests are summarized in Table 1. The initial dissolved-oxygen concentrations are close to 1 mg/L from the degassing approach used to fill the tanks. The only exception is seen at the CD level (within three inches of the water surface) that is presumably from significant diffusion from the atmosphere (the bioventing tank was not sealed at the surface). Overall, the bioventing process increased dissolved-oxygen concentrations in the tank. After the biovents, the dissolved oxygen changes considerably at almost every level affected by the drawdown event. More oxygen was delivered at higher levels in the tank with a maximum increase in dissolved oxygen observed within a foot of the high water mark (108-234 % increase). At level NO (the low water mark for the drawdown event), no significant change in dissolved-oxygen level is observed. At the top of the tank (CD), a 79% average change is seen. This relatively small change is due to the high, dissolved-oxygen concentrations present at this level before the initiation of the biovents. Final dissolved-oxygen concentrations increased as high as 4.26 mg/L, which is well within the range for aerobic

Table 1. Average change in dissolved oxygen after two bioventing events before the diesel oil spill. Sampling ports are arranged based on height in the tank.

Port		Initial DO (mg/L)	Final DO (mg/L)	Change % (mg/L)	% Change	Average % Horizontal
Vertical	Horizontal					
CD	2/3	3.71	4.57	0.86	23	79
CD	7/8	0.87	2.11	1.24	143	
CD	15/16	1.46	2.49	1.03	71	
DE	-1/0	1.46	4.26	2.8	192	162
DE	10.5/11	1.67	3.85	2.18	131	
EF	5.5/6	1.4	3.9	2.5	179	108
EF	13/14	1.26	1.72	0.46	37	
GH	6/7	0.67	3.81	3.14	469	234
GH	14/15	1.05	1.03	-0.02	-2	
IJ	4/5	1.35	1.91	0.56	42	47
IJ	10.5/11	1.65	2.51	0.86	52	
KL	3/4	0.94	1.22	0.28	30	25
KL	9/10	0.85	1.3	0.45	53	
KL	15/16	1.82	1.68	-0.14	-8	
NO	-1/0	0.88	1.05	0.17	19	-2
NO	7/8	1.43	1.45	0.02	1	
NO	16/17	1.33	0.97	-0.36	-27	

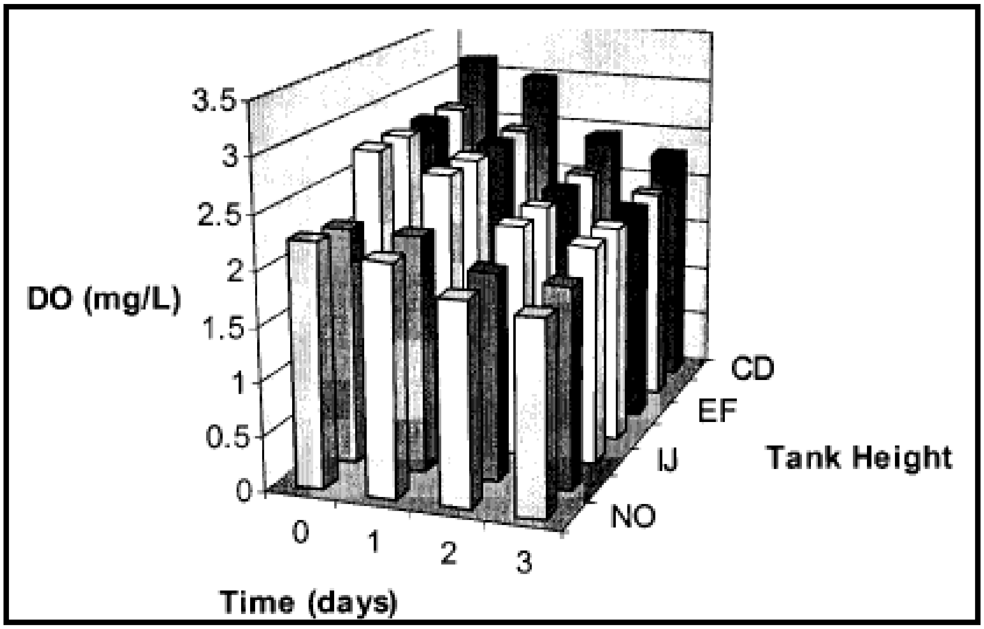

Figure 4. Dissolved-oxygen uptake after bioventing in pre-oil spilled tank as a function of the tank height.

respiration. Table 1 also illustrates the large degree of heterogeneity in oxygen delivery. Although the overall trend is toward increased oxygen delivery with increasing height within the drawdown zone, the amount of oxygen delivered to discreet areas of the soil will vary greatly.

After restoring the water table to the original level and measuring dissolved oxygen, the tank was allowed to remain static over the course of three to seven days. During this time, dissolved oxygen was measured to assess the rate of oxygen depletion and diffusion within the tank. Two effects were possible. First, significant biological activity in the tank could lead to significant decreases in dissolved oxygen over this time period (based on rates observed in batch studies on the order of days). Second, diffusion of dissolved oxygen could lead to delivery of the dissolved oxygen through the soil heterogeneities. Results from one of these tests are shown in Figure 4, as an average dissolved-oxygen concentration for the horizontal cross section plotted over time.

A slow decrease in dissolved oxygen is observed at all heights within the tank over three days. This indicates that a small degree of biological activity is occurring. This activity could be based on degradation of the residual diesel from the site soil and/or from degradation of organic matter inherent to the soil. An establishment of equilibrium is also apparent due to the diffusion of oxygen. After three days, the discrepancies in dissolved-oxygen level between the different tank heights (2.1-3.1 mg/L range at zero days) decreases (1.7-2.1 mg/L range after three days).

Two additional biovent events were conducted after spilling diesel oil onto the tank. The addition of oil has the potential to change the permeability of the soil to oxygen due to the presence of oil blobs and fingers. These oil morphologies can create additional barriers to permeability by stagnating air flow through the pore spaces. This effect can be compounded in the presence of preferential pathways because oil will tend to fill these spaces, thereby forcing air flow through less permeable pore spaces in the soil.

The change in dissolved oxygen after a bioventing event (a single drawdown and restoration of the water table) was measured after the diesel oil was spilled onto the tank. The average results of the two bioventing tests are summarized in Table 2. After initial DO measurement, the water table was drawn down and restored. The DO was then measured and is reported in Table 2, along with the change in DO concentration, percent change for each sampling port, and average percent change for each horizontal cross section.

As with pre-oil bioventing, the overall DO concentration increased after a single biovent. The magnitude of the increase in DO concentration is very similar to the magnitude increase seen in pre-oil spill bioventing. The average increase in DO concentration from pre-oil spill biovents at levels above the low water mark (not including the NO horizontal cross section) is 1.157 mg/L. The average increase in DO concentration from post-oil spill biovents at levels above the low water mark (not including

Table 2. Average change in dissolved oxygen after bioventing events following the diesel oil spill. Sampling ports are arranged based on height in the tank.

Port		Initial DO (mg/L)	Final DO (mg/L)	Change % (mg/L)	% Change	Average % Horizontal
Vertical	Horizontal					
CD	2/3	1.1	2.71	1.61	146	163
CD	7/8	1.67	3.76	2.09	125	
CD	15/16	0.99	3.16	2.17	219	
DE	-1/0	1.46	2.62	1.16	79	99
DE	10.5/11	1.17	2.56	1.39	119	
EF	5.5/6	2.1	1.87	-0.23	-11	53
EF	13/14	1.22	2.63	1.41	116	
GH	6/7	1.32	1.87	0.55	42	39
GH	14/15	1.52	2.05	0.53	35	
IJ	4/5	1.24	1.86	0.62	50	127
IJ	10.5/11	1.05	3.19	2.14	204	
KL	3/4	0.94	1.97	1.03	110	240
KL	9/10	0.53	2.49	1.96	370	
KL	15/16	1	2	1	100	
NO	-1/0	1.06	1.22	0.16	15	34
NO	7/8	1.15	1.3	0.15	13	
NO	16/17	0.96	1.68	0.72	75	

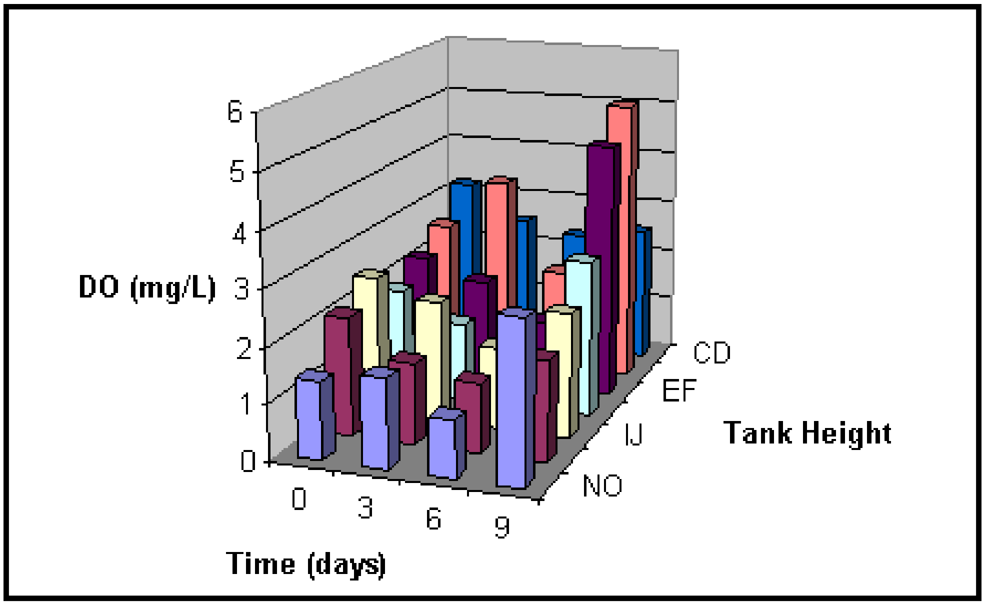

Figure 5. Dissolved-oxygen uptake after bioventing in post-oil spilled tank as a function of the tank height.

the NO horizontal cross section) is 1.245 mg/L. The results suggest that the diesel oil does not significantly alter the overall delivery of oxygen into the smear zone. Although the final concentration of DO is somewhat lower in the post-oil spill tests, this is due to slightly lower initial concentrations. DO concentrations in the post-oil spill experiments reached concentrations as high as 3.76 mg/L, which is within the domain of aerobic metabolism. Bioventing tests after the oil spill show a different distribution of oxygen delivery, with the largest percent change occurring deep within the tank. However, this could be due to the fact that a section of the tank was repacked between experiments. The result suggests that the effects of heterogeneity and preferential pathways to air flow have a more significant effect than the depth of the soil. DO concentrations at the low water mark show a relatively small change, although it is significantly larger than observed in pre-oil spill bioventing.

After restoring the water table to the original level and measuring dissolved oxygen, the tank was allowed to remain static over the course of six to nine days. During this time, dissolved oxygen was measured to assess the rate of oxygen depletion and diffusion within the tank. The results from one of these tests is shown in Figure 5 as an average dissolved-oxygen concentration for the horizontal cross section plotted over time. A decrease in dissolved oxygen is observed at all heights within the tank over the first six days. The post-oil spill uptake rate is somewhat faster than observed in pre-oil spill experiments. This oxygen uptake rate is presumably due to the larger substrate concentration available from the spilled oil. However, after nine days, the oxygen concentration increases dramatically. The cause for this increase is unknown. Only one of the post-oil spill experiments was allowed to remain static over nine days, so the result has not been reproduced. An establishment of equilibrium is also apparent due to the diffusion of oxygen. After six days, the discrepancies in dissolved-oxygen level between the different tank heights (1.1-3.8 mg/L range at zero days) decreases (0.8-2.1 mg/L range after three days).

The intermediate-scale tanks are designed to allow visual inspections of the oil distribution in the tank as well as to allow sampling for sheen. Visual observations during the bioventing process showed clear signs for the effects of heterogeneity. First, during drawdown and refilling, the establishment of preferential pathways for air and water flow were evident. Fingering of water in both directions indicated that flow occurs through discreet pathways. The result of the flow pattern suggests that residual blobs of water and/or oil will rely on diffusion of oxygen from these preferential paths. This result suggests that estimations of degradation time, based on large-scale delivery of oxygen, will be optimistic. The actual times required for diesel degradation will likely be longer than predicted by models that do not account for the soil heterogeneities.

Samples extracted from the intermediate-scale tank were observed for the presence of sheen. Of particular interest was whether blobs and fingers of oil moved after bioventing. It was apparent that although the diesel does migrate during the water movement, it tends to return to the same regions after re-establishment of the water table. This effect is presumably due to local heterogeneities that tend to hold the oil better than surrounding regions.

Biosparging

The change in dissolved oxygen after a biosparging event (a one-hour injection of air at inlet pressure of 4 psi) was measured before the diesel oil was spilled onto the tank. The results of the two biosparging tests are summarized in Table 3. After the biosparges, the dissolved oxygen changes considerably within a definable

Table 3. Average change in dissolved oxygen after two biosparging events before the diesel oil spill. Sampling ports are arranged based on height in the tank.

Port		Initial DO (mg/L)	Final DO (mg/L)	Change % (mg/L)	% Change
Vertical	Horizontal				
CD	2/3	4.29	6.32	2.03	47
CD	7/8	3.14	6.84	3.7	118
CD	15/16	2.32	2.33	0.01	0
DE	-1/0	4.1	2.49	-1.61	-39
DE	10.5/11	0.87	5.44	4.57	525
EF	5.5/6	1.8	1.8	0	0
EF	13/14	1.63	4.21	2.58	158
GH	6/7	3.19	5.08	1.89	59
GH	14/15	0.99	5.21	4.22	426
IJ	4/5	3.01	3.85	0.84	28
IJ	10.5/11	0.79	4.18	3.39	429
KL	3/4	1.63	1.92	0.29	18
KL	9/10	1.44	5.9	4.46	310
KL	15/16	2.72	6.69	3.97	146
NO	-1/0	2.16	2.22	0.06	3
NO	7/8	4.09	4.08	-0.01	0
NO	16/17	2.92	3.59	0.67	23

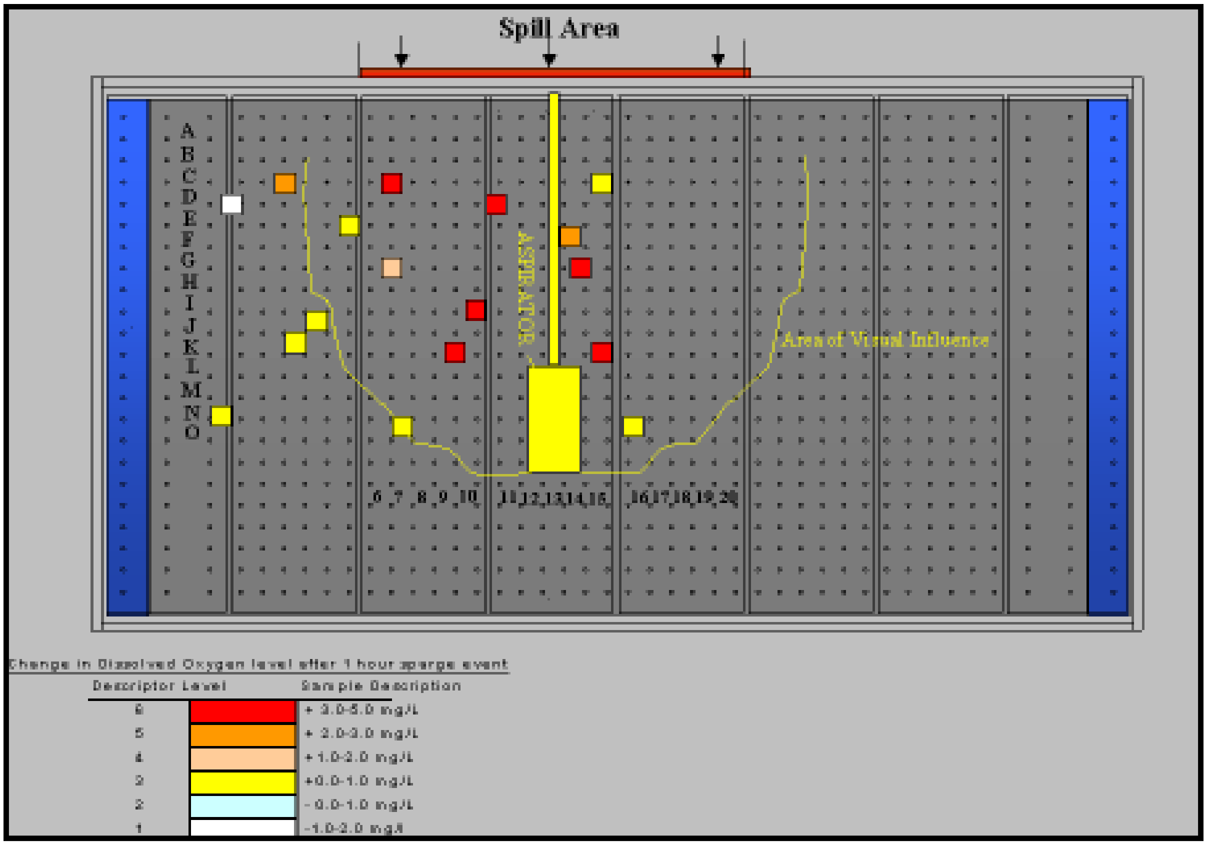

Figure 6. Average change in dissolved oxygen after two bioventing events before the diesel oil spill. Line represents injected-air area of visible influence based on visual obervation of air passage. Shades are described below the tank schematic.

area of visible influence. It is apparent that sparging has a larger overall effect on dissolved-oxygen concentrations than bioventing under similar circumstances (Table 1). Higher dissolved oxygen is typically delivered at sampling ports closer to the aspirator (located at 11/12), as expected based on the oxygen delivery profile. Dissolved-oxygen concentration increased as much as 4.5 mg/L. Ports well outside of the area of visible influence demonstrated significantly lower increases in dissolved oxygen (CD 15/16, DE –1/0, NO –1/0) with two exceptions (KL 15/16 and NO 16/17). It is believed, based on the large increases in dissolved oxygen outside of the area of visible influence and based on the very large preferential pathway effect, that air pathways are extending well beyond the largest area of visible influence. The data from Table 3 is reproduced in the context of the tank sampling ports in Figure 6, along with the area of visible influence for air sparging based on visual assessment. Figure 6 illustrates the large degree of heterogeneity in oxygen delivery. This heterogeneity is similar to that observed in bioventing tests, suggesting that the phenomena are dependent on soil characteristics and not just the air-delivery technique. Although the overall trend is toward increased oxygen delivery with decreasing distance from the aspirator well, the amount of oxygen delivered to discreet areas of the soil will vary greatly.

After restoring the water table to the original level and measuring dissolved oxygen, the tank was allowed to remain static over the course of three days. Results from one of the tests are shown in Table 4 for each sampling port over the three-day period. A slow decrease in dissolved oxygen is observed at all sampling ports within the tank over three days. This rate of oxygen depletion is faster than those reported for lower initial oxygen concentrations from biovent tests. This indicates that a small amount of biological activity is occurring.

The change in dissolved oxygen after a biosparging event (a one-hour air injection of 4 psi inlet pressure) was measured after the diesel oil was spilled onto the tank. Initial dissolved-oxygen concentrations are somewhat higher than 1 mg/L, reflecting the use of existing water in the tank rather than new degassed water. This measure was taken as a result of malfunctions in the degas apparatus. After initial DO measurement, air was injected for one hour. The DO was then measured and is reported in Table 5, along with the change in DO concentration and percent change for each sampling port. The magnitude of the increase in DO concentration is slightly lower (1.66 mg/L average increase) than seen for pre-oil spill biosparges (2.16 mg/L average increase). This reflects the higher initial dissolved-oxygen

Table 4. Dissolved-oxygen uptake after biosparging in pre-oil spilled tank as a function of each sampling port.

Port		Initial DO (mg/L)	1-day DO (mg/L)	2-day DO (mg/L)	3-day DO (mg/L)
Vertical	Horizontal				
CD	2/3	6.32	5.41	4.52	3.71
CD	7/8	6.84	4.10	2.18	0.87
CD	15/16	2.33	2.10	1.86	1.46
DE	-1/0	2.49	2.16	1.54	1.46
DE	10.5/11	5.44	4.16	2.49	1.67
EF	5.5/6	1.8	1.77	1.42	1.4
EF	13/14	4.21	3.46	2.44	1.26
GH	6/7	5.08	4.36	2.67	0.67
GH	14/15	5.21	3.86	2.06	1.05
IJ	4/5	3.85	2.46	1.27	1.35
IJ	10.5/11	4.18	3.54	2.06	1.65
KL	3/4	1.92	1.55	1.09	0.94
KL	9/10	5.9	4.19	2.28	0.85
KL	15/16	6.69	5.10	3.49	1.82
NO	-1/0	2.22	1.86	1.14	0.88
NO	7/8	4.08	3.26	2.37	1.43
NO	16/17	3.59	3.11	1.52	1.33

concentrations. Results suggest that the diesel oil does not significantly alter the overall delivery of oxygen into the smear zone. DO concentrations in the post-oil spill experiments reached concentrations as high as 7.92 mg/L. This large, dissolved-oxygen concentration suggests that an equivalent time of biosparging yields significantly higher dissolved oxygen than bioventing tests.

During each of the sparging events, large pathways for preferential air flow were present along the side wall of the intermediate tank. This result is commonly observed in biosparging applications (Suthersan, 1997). As described in bioventing applications, the result of the flow pattern suggests that residual blobs of water and/or oil will rely on diffusion of oxygen from these preferential paths. However, all areas within the area of visible influence show increased DO. This indicates that the deliverability of DO occurs throughout the area of visible influence. Second, some areas outside of the area of visible influence show increased DO. Therefore, predictions of oxygen delivery could be conservative due to oxygen delivery outside of the predicted area of visible influence.

The delivery of oxygen to sampling ports outside of the area of visible influence is due to a large number of horizontal, preferential pathways. In some cases, horizontal pathways were observed to extend from the aspirator tip, along the entire length of the tank, to the gravel wells set at either end. These horizontal pathways are

Table 5. Average change in dissolved oxygen after one biosparging event following the diesel oil spill. Sampling ports are arranged based on height in the tank.

Port		Initial DO (mg/L)	Final DO (mg/L)	Change % (mg/L)	% Change
Vertical	Horizontal				
CD	2/3	3.02	5.29	2.27	75
CD	7/8	1.98	4.19	2.21	112
CD	15/16	2.51	2.79	0.28	11
DE	-1/0	4.24	3.43	-0.81	-19
DE	10.5/11	6.24	7.92	1.68	27
EF	5.5/6	6.26	7.3	1.04	17
EF	13/14	3.16	3.55	0.39	12
GH	6/7	3.12	6.38	3.26	104
GH	14/15	2.58	3.46	0.88	34
IJ	4/5	1.84	3.26	1.42	77
IJ	10.5/11	2.66	7.47	4.81	181
KL	3/4	1.59	2.06	0.47	30
KL	9/10	1.90	5.72	3.82	201
KL	15/16	1.95	3.51	1.56	80
NO	-1/0	3.45	3.16	-0.29	-8
NO	7/8	2.31	3.11	0.8	35
NO	16/17	2.94	3.72	0.78	27

presumably due to large-scale heterogeneities and will increase the overall area of soil to which oxygen can be delivered.

During sparging tests (with inlet pressure of 4 psi), water in the saturated zone ponded above the soil surface to a depth of three inches. This ponding has been observed for sites with shallow groundwater tables (Suthersan, 1997). The result is potentially increased smearing in the vadose zone, as well as collection and treatment of ponded water for intermediate-scale tests. Oil movement based on sheen analysis showed similar characteristics to those described after biovent tests.

IMPLICATIONS AND CONCLUSIONS

The intermediate-scale test tank was established to determine the effectiveness of oxygen delivery using simulated, pulsed bioventing/ water drawdown or biosparging technologies. Results from the measurement of dissolved oxygen show that bioventing can effectively increase the dissolved-oxygen concentration. A single biovent event lasting for one hour was capable of increasing dissolved-oxygen levels by approximately 1.5 mg/L in oil-free and oil-contaminated soil. A single biosparge event lasting for one hour was capable of increasing dissolved-oxygen levels by approximately 1.66 mg/L in oil-free and 2.16 mg/L in oil-contaminated soil. Moreover, within the one-hour period, dissolved-oxygen concentrations were observed as high as 7.92 mg/L, which is close to saturation of water under test conditions. The resulting DO concentration decreased after both bioventing and biosparging within three days. Both of these sets of results constitute significant increases in dissolved-oxygen concentration over a short period of time. The resulting DO concentration decreased after the bioventing within three to six days. The optimal periods for pumping and exact DO delivery will vary from intermediate to field scale.

Several factors affecting the efficiency of the technologies are also indicated by the results. First, heterogeneities in the system have a large impact on the amount of oxygen deliverable. Formation of preferential pathways and resulting blobs and finger formations can decrease the effective dissolved oxygen on a microscale. This factor is reflected in both visual assessments of sheen presence and flow characteristics, as well as the differences in dissolved-oxygen concentration seen in horizontal cross sections. The result will be a slower actual degradation rate than predicted, based on macro-scale samples of dissolved oxygen

In the case of biosparging, every sample taken from within the visual area of influence demonstrates increased dissolved-oxygen concentration, indicating that although the heterogeneities affect air flow, the overall effect is a rapid increase in dissolved oxygen. Moreover, the presence of preferential flow paths results in a large amount of horizontal channels. This will increase the effective area of dissolved-oxygen influence and result in larger zones of oxygenation. The biosparging results also indicate that, despite the smaller size of intermediate-scale tests, the residence time of air bubbles passing through heterogeneous soil is sufficient to allow significant diffusion of oxygen from the gas phase to the bulk aqueous medium.

The amount of dissolved oxygen delivered is highly dependent on the methodology of the bioventing system (frequency of pumping, introduction of pumped air, depth of smear zone, etc.). All of these factors influence the biodegradation rate of diesel by aerobic micro-organisms. Other factors, such as the addition of nutrients, changes in the microbial population, presence of alternate substrates, and presence of large concentrations of iron in the subsurface, will also impact biodegradation rates. Finally, oxygen delivery in the unsaturated and dewatered zones was not considered due to limitations of the intermediate-scale system. Activity in these zones is potentially significant.

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