

REMOVAL OF DISSOLVED- AND FREE-PHASE BENZENE POOLS FROM GROUND WATER USING IN SITU AIR SPARGING

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ABSTRACT: This paper presents the results of a laboratory investigation performed to study the use of air sparging to remediate dissolved-phase and free-phase [or non-aqueous-phase liquid (NAPL)-phase] benzene pools from ground water. The specific objectives of the study were (1) to assess how air injection rate affects the mass transfer and transport of dissolved- and NAPL-phase pools; and (2) to determine the effect of ground-water flow on the removal of dissolved- and NAPL-phase pools during the application of air sparging. A total of five 2D physical model tests were performed in a homogeneous coarse sand profile subjected to both static ground water and ground-water flow conditions. Three different air injection rates were used in a static ground-water condition, and two different air flow rates were used in soil profiles subjected to ground-water flow (hydraulic gradient = 0.011). All tests were performed with similar initial dissolved- and NAPL-phase benzene conditions. Injected air traveled within a parabolic zone of influence (in channel mode) when subjected to both static ground water and ground-water flow conditions, indicating that ground-water flow (for the ground-water velocities tested) did not affect the injected air zone of influence. An increase in air injection rate led to faster contaminant removal; however, at higher air injection rates, a threshold rate of removal was reached above which further increases in injection rate are a waste of effort. Additionally, air injected into the soil profile reduced the hydraulic conductivity within the zone of influence. This in turn led to lower ground-water flow rates, allowing for effective interception and treatment of a migrating NAPL plume. Higher air injection rates led to further reductions in hydraulic conductivity, allowing for substantial control of the NAPL plume in the downgradient direction. Overall, this study showed that air sparging can be used to effectively remediate dissolved- and NAPL-phase benzene.

INTRODUCTION

Air sparging is a technique that has proven to be efficient for the remediation of saturated soils and ground water that have been contaminated with volatile organic compounds (Ardito and Billings 1990; Marley et al. 1992; Johnson et al. 1993; Leonard and Brown 1994; Reddy et al. 1995; Reddy and Adams 1998). During air sparging, a gas, usually air, is injected into the subsurface below the lowest known point of contamination. Due to effects of buoyancy, the injected air will begin to rise through the saturated zone toward the surface. Through a variety of mass transfer processes, the contamination is either transferred into the migrating air or oxygen is transferred into the subsurface, effectively stripping or assisting in the degradation of the contamination. As the contaminant-laden air continues to rise, it encounters the vadose zone, where it is captured using a soil vapor extraction system. By applying a vacuum to the subsurface, the soil vapor extraction system is able to control vapor movement by inducing a pressure gradient toward the extraction wells, which prevents vapor migration into uncontaminated soil regions. Once extracted, the contaminated air may be treated using conventional methods such as carbon filters or combustion.

When volatile organic contaminants are released into the saturated subsurface, they commonly exist in dissolved phase as well as free or non-aqueous-phase liquid (NAPL) phase. Volatile organic compounds that commonly contribute to subsurface contamination (e.g., petroleum compounds and chlorinated solvents) often have low water solubilities; therefore,

the contaminant often exists in the NAPL phase. Contamination that has dissolved into the ground-water phase effectively becomes a ground-water constituent and therefore will migrate with ground-water flow. When contamination exists in a NAPL phase, ground-water flow may still induce migration through different mass transport mechanisms, including advection. Additionally, if the contaminant is lighter than water, commonly referred to as light NAPLs (LNAPLs), the contaminant may float on the water table, forming an NAPL-phase pool. When water table levels fluctuate, the pool may be smeared, contributing to contaminant entrapment within soil pores.

Many studies performed to assess air sparging, involving either the evaluation of field studies, physical models, or mathematical models, have assumed that contamination exists as dissolved phase. However, dissolved- and NAPL-phase contaminant transport and removal may be markedly different. A number of previous studies have focused on NAPL transport within the subsurface due to both gravity-induced infiltration and ground-water flow. However, little research has been performed to assess how air injection affects the transport of NAPL-phase contamination within the subsurface as well as the remediation of dissolved- and NAPL-phase pools, especially when ground-water flow is occurring. The relative contributions of injected air and ground-water flow toward NAPL-phase contamination partitioning, transport, and removal must also be studied to understand how multiple fluid movement affects air sparging. Additionally, to optimize field system design and performance, the mass transfer/transport mechanisms that are important in NAPL-phase remediation during air sparging must be carefully assessed. To correctly assess and predict the performance of air sparging, the interaction of these different fluid phases as well as contribution of the different remedial phenomena must be carefully studied.

The objectives of this study are (1) to assess how air injection rate affects the mass transfer and transport of dissolved- and NAPL-phase pools; and (2) to determine the effect of ground-water flow on the removal of dissolved- and NAPL-phase pools during the application of air sparging. To accom-

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plish these objectives, controlled 2D physical model tests were performed with dissolved- and NAPL-phase pools in coarse sand soil profiles. The first series of tests was conducted with three different air injection rates under a static ground-water condition. The second series of tests was performed with two different air injection rates under ground-water flow conditions. The results of these tests were utilized to assess the removal of dissolved- and NAPL-phase pools using air sparging.

EXPERIMENTAL PROGRAM

Aquifer Simulation Apparatus

A 2D aquifer simulation test apparatus, shown in Fig. 1, has been developed to study spatially dependent variables that may affect air sparging. The large dimensions of the test apparatus allow for the simulation of a soil profile. The simulator also offers flexibility by allowing better control of contaminant placement and ground-water flow. The tank is made of Plexiglas and measures 111 cm in length, 72 cm in height, and 10 cm in width. The interior of the tank consists of three compartments; a soil chamber measuring 91 cm in length is centered within the tank and is flanked by two ground-water reservoirs, measuring 10 cm in length each. The two water reservoirs on either side of the soil chamber are connected to constant-head clean water source reservoirs. The source reservoirs are adjustable in height, allowing for a specific head to be maintained in each reservoir. Additionally, the source reservoirs may be adjusted to create a hydraulic gradient across the tank, thereby inducing ground-water flow. The tank reservoirs are separated from the soil chamber by a geotextile-lined heavy-gauge perforated stainless steel screen, allowing water to freely enter or exit the soil chamber but preventing

soil particles from entering the water reservoirs. On the face of the soil chamber, 20 sampling ports are arranged in four rows of five, each protruding into the soil chamber. The ports allow for the sampling of pore water from the soil profile throughout the course of a test.

Materials

A uniform coarse sand obtained from the U.S. Silica Company (U.S. Silica designation 20/40 fraction) was used as the test soil for this research. The sand is poorly graded, with a $D_{10} = 0.43$ mm and a $D_{50} = 0.55$ mm. The hydraulic conductivity of the sand is 4.64×10^{-2} cm/s and the porosity under test conditions is 0.4. Benzene (Fisher Scientific B245-500, Thiophene-free, certified by American Chemical Society, Washington, D.C.) was chosen as the representative LNAPL because it is a major constituent of gasoline and other petroleum products and is often encountered at contaminated sites.

Testing Program

All tests were performed using homogeneous coarse sand profiles. Three different tests were performed under a static ground-water condition at different air injection rates: 1,250 mL/min (referred to as low air flow), 2,500 mL/min (medium air flow), and 4,750 mL/min (high air flow). All three air flow rates were injected under an entry pressure of 4.5–5.0 kPa. Two additional tests were performed subjected to ground-water flow with a hydraulic gradient of 0.011 utilizing an air injection rate of 2,500 mL/min (referred to as low air flow) in one test and 4,750 mL/min (high air flow) in the second test.

Testing Procedure

When performing a test, the soil profile was prepared in the same manner as in previous investigations utilizing the 2D

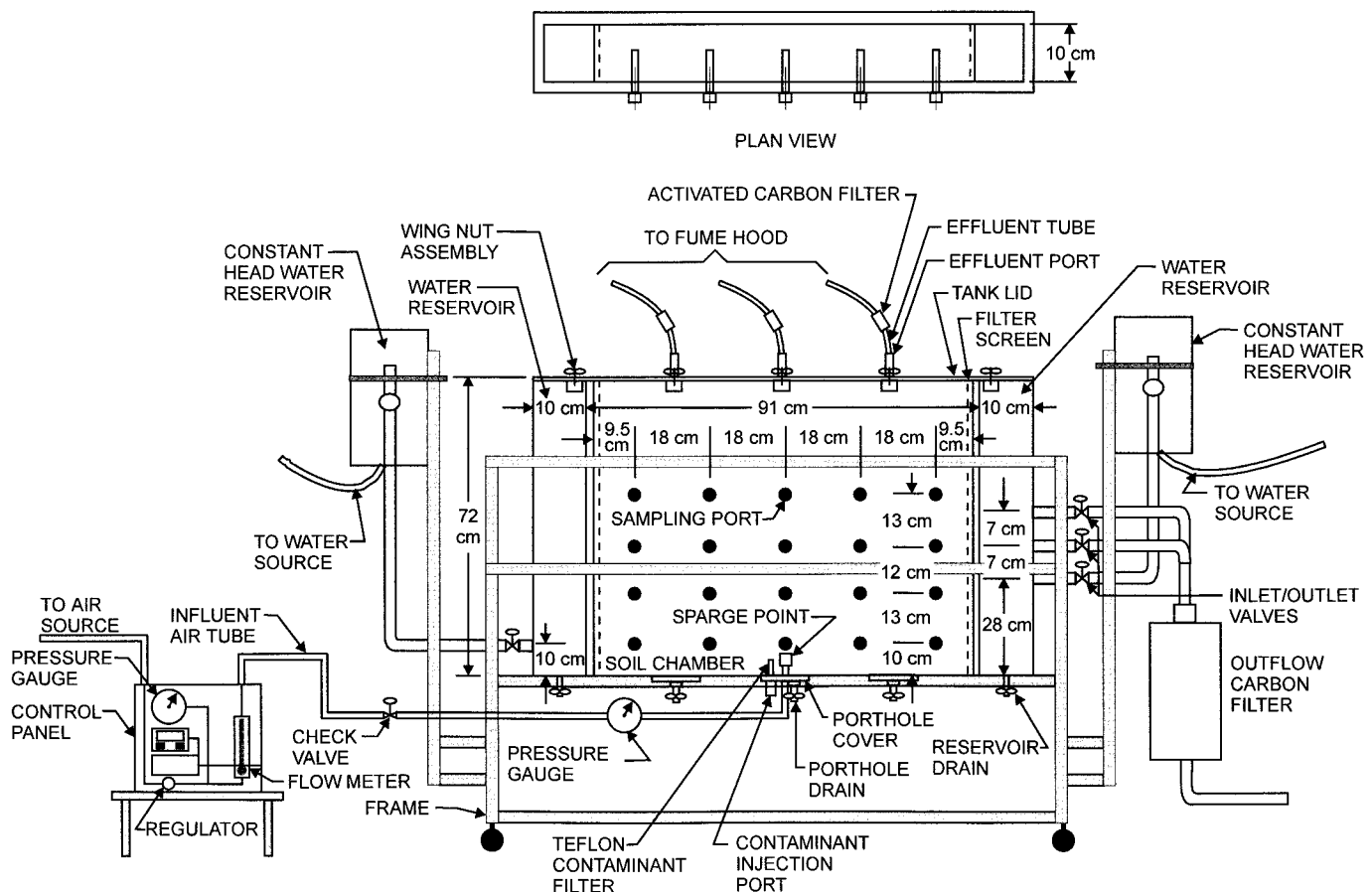


FIG. 1. Two-Dimensional Aquifer Simulation Apparatus

testing apparatus. Coarse sand was placed through the top of the apparatus using a consistent drop height. The height of the resulting profile as well as the mass of the placed soil were recorded. A high concentration, NAPL-phase benzene solution was mixed by injecting 3 mL of pure benzene into 940 mL of deionized water contained within a special sealed no-head injection device (Reddy and Adams 1998). The mixture was placed on a magnetic stirring plate and mixed for approximately 1 h.

Following soil placement, a portion of the soil profile was saturated through water infiltration from the water reservoirs (Fig. 1). The profile was saturated to a height just below the center row of sampling ports, forming a water table within the soil profile. The contaminant mixture was injected into the soil profile just above the water table through a slotted stainless steel probe placed into the soil through the top of the tank. This injection method allowed for the creation of a contaminant pool encompassing Ports S1 and S2, as shown in Fig. 2. This contaminant pool simulates a subsurface LNAPL release that has encountered the water table. Once the contaminant zone was established, the remainder of the soil profile was saturated, creating a smearing effect of the NAPL-phase benzene characteristic of water table fluctuation. The tank cover was fastened and sealed in place, and effluent air tubes fitted with activated carbon filter tubes were fastened to the tank cover effluent ports. The initial benzene concentration profile was determined through pore-water sampling and analysis. Once the soil profile had been saturated, air injection began. Flow rate and injection pressures were controlled with the use of the control panels, and an electronic timer was used to monitor the time of air injection. At regularly scheduled times during the test, 2 μ L samples of pore water were extracted from the soil profile through the sampling ports using gas-tight syringes. The samples were drawn throughout the test to monitor progress. The benzene mass remaining in the soil was calculated based on these samples. Although all ports within the soil profile were monitored and analyzed, only ports with detectable concentrations of benzene are reported within this test. In addition, the ORBO tubes were changed at regular intervals

to monitor the amount of contaminant volatilized during a specific time interval. The tubes were sealed and refrigerated to prevent any premature desorption from the charcoal within the tubes. The injected air flow patterns were visually observed and carefully sketched for each test.

To study the effect of ground-water flow, a ground-water gradient was established across the soil profile. The water reservoirs were adjusted to provide the desired water level within the tank reservoirs. The height difference in the water levels between the influent and effluent reservoirs was maintained at 1 cm, providing a gradient ($\Delta h/l$) of 0.011 over the 91-cm length of the soil profile. Both the water within the outlet reservoir and the effluent flow from the test apparatus were analyzed for benzene regularly to determine the extent of benzene migration and/or removal as a result of the migrating ground water. The effluent ground-water flow passed through a carbon filter to remove benzene before discharging.

To assess the mass transfer and removal during the experiments, chemical analysis of the extracted pore water, the water within the outflow reservoir, the effluent flow from the apparatus, and the ORBO tubes were performed. The chemical analysis was performed using gas chromatography.

RESULTS AND ANALYSIS

Low Air Flow Injection under Static Ground Water

For the first test, an initial benzene concentration of 1,300 mg/L was detected in the upper region, or Port S1, and an initial benzene concentration of 180 mg/L was detected in the lower region, or Port S2. Then air was injected at a flow rate of 1,250 mL/min. The observed zone of influence and the air flow pattern within the homogeneous coarse sand profile are shown in Fig. 3. The zone of influence completely envelops the contaminated zone.

Fig. 4 shows the concentration changes in the dissolved- and NAPL-phase pool (Ports S1 and S2) with time. After an hour of air injection, the benzene concentration within the lower region (Port S2) dropped to 30 mg/L, indicating substantial benzene removal. However, the concentration in-

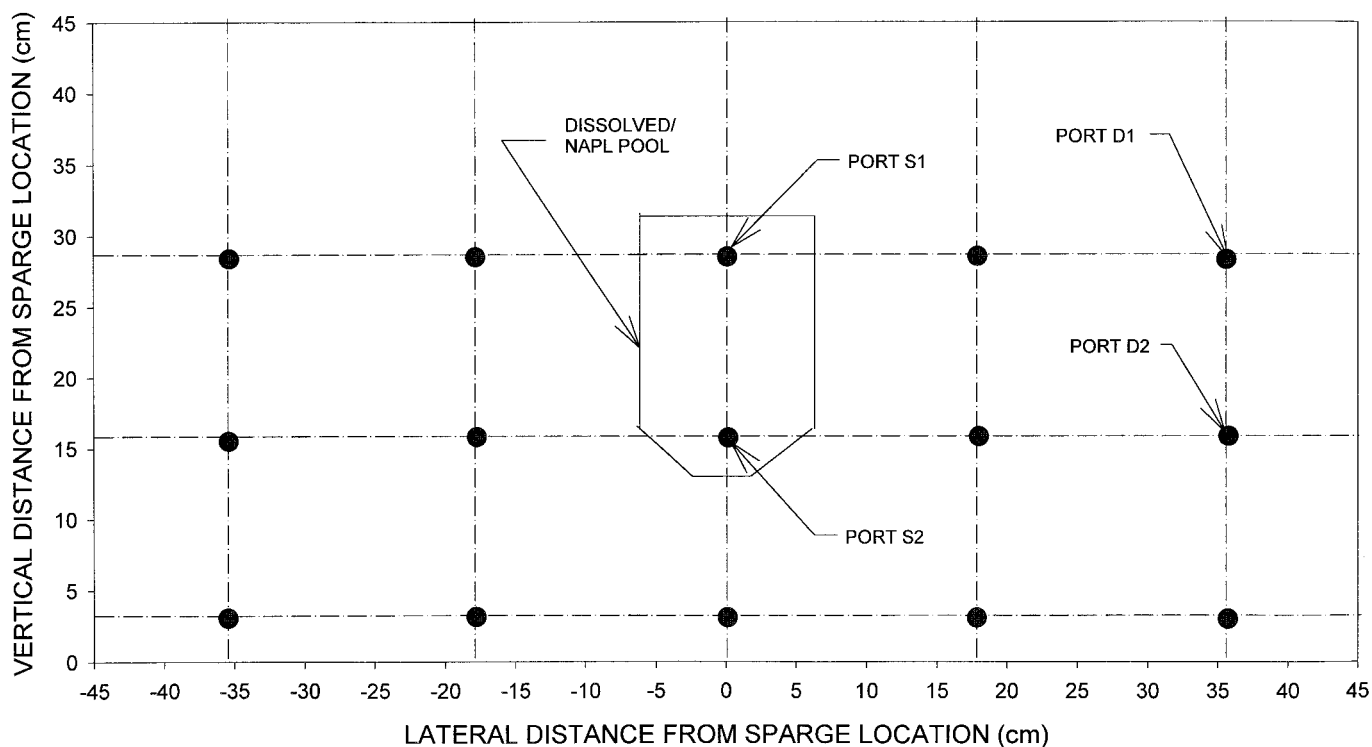


FIG. 2. Dissolved- and NAPL-Phase Pool within 2D Aquifer Simulation Apparatus

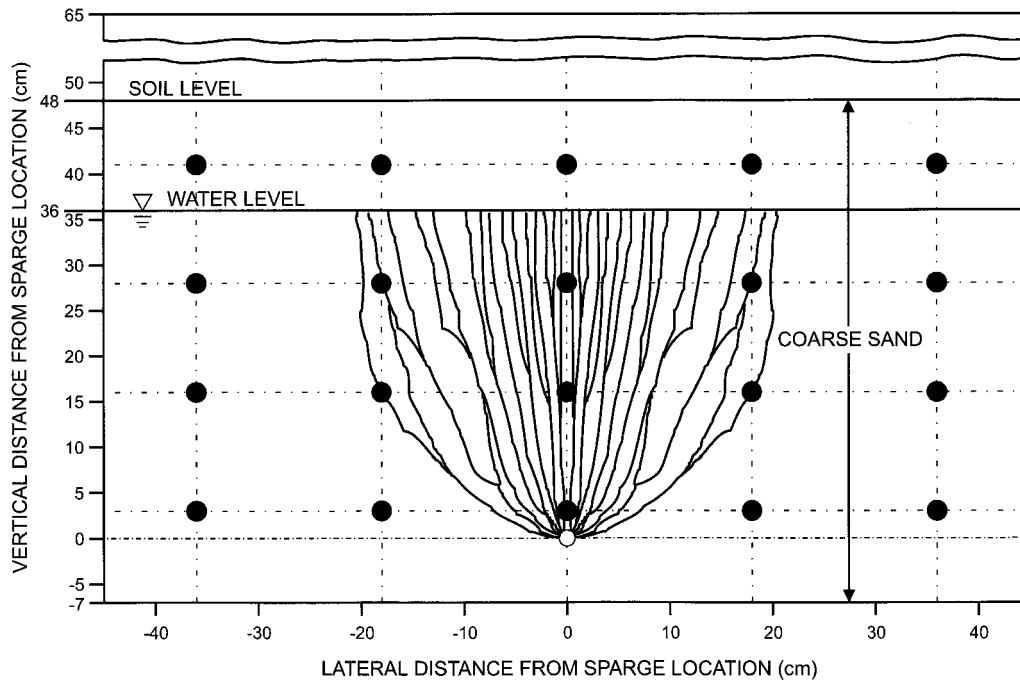


FIG. 3. Air Flow Pattern; Coarse Sand

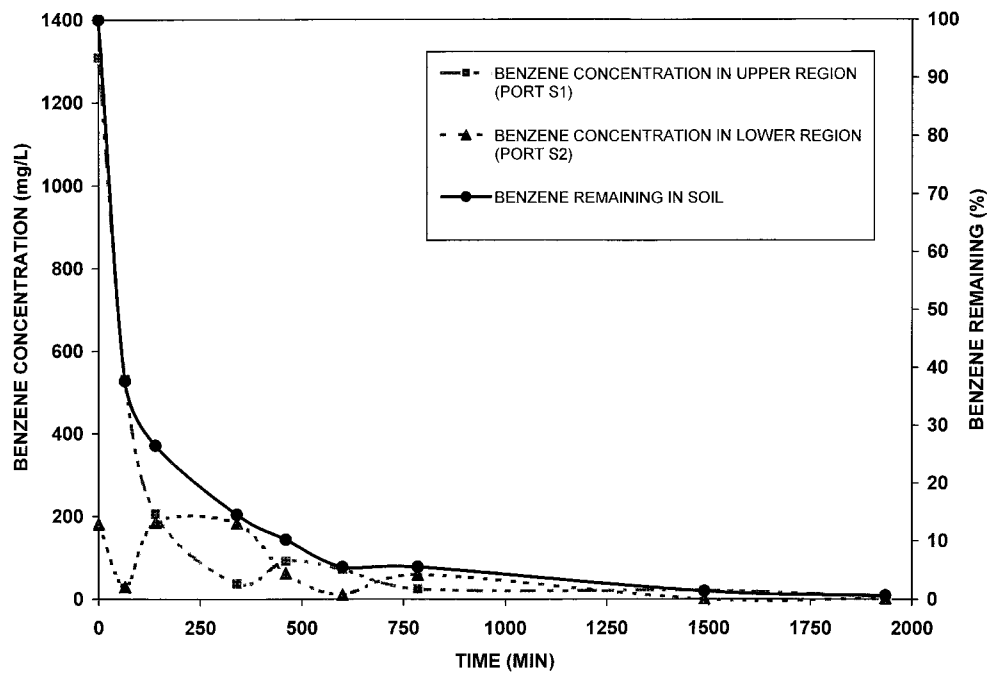


FIG. 4. Benzene Remaining versus Time; Air Flow Rate = 1,250 mL/min

creased to 180 mg/L at a later sampling due to benzene migration from surrounding regions. Within the upper region (Port S1), substantial removal also occurred, as the benzene concentration dropped from 1,300 to 200 mg/L following 2 h of air injection. This region was also subjected to concentration fluctuation at later stages of air injection. Fig. 4 also shows the overall benzene mass remaining in the source zone with time. Nearly 60% of the initial benzene mass was removed within the first hour of air injection. At later times, however, the rate of benzene removal decreased. With further air injection, complete contaminant removal was achieved; 95% of the initial benzene mass was removed within an elapsed time of 600 min, and benzene concentrations were below detection limits following 1,900 min of air injection.

The fluctuating benzene concentrations in the source zone (Fig. 4) are the direct result of both benzene phase distribution and mixing induced by the injected air. Although a major portion of the initial benzene mass was able to partition from either the NAPL or dissolved phase into the vapor phase for removal, a portion of the contaminant may have been trapped within soil pores away from the migrating air. Immobile NAPL acts as a source for further dissolved-phase contamination, resulting in enhanced retention and delayed removal (tailing). Near the NAPL source, the dissolved benzene concentration fluctuates due to agitation, leading to dissolution-induced mobilization and removal of trapped and sorbed benzene. The lower air flow used during this test resulted in a lower air saturation due to lower air channel density. Less air may also

have resulted in less mechanical dispersion in the pore water within the zone of influence. Mechanical dispersion is a mass transport mechanism important in the removal of NAPL-phase benzene contamination. When NAPL-phase benzene is trapped within soil pores that are not in the vicinity of an air channel, dispersion-induced dissolution is required for contamination removal from the soil pore. Air injection-induced mechanical dispersion results in ground-water agitation and movement, aiding dissolution. As the injected air rises toward the surface, local turbulence occurs, reducing the thickness of the quiescent boundary layers around NAPL-phase benzene ganglia and increasing dissolution (Wilson et al. 1994). After partitioning into the mobile dissolved phase, the benzene is able to diffuse toward an air channel. Upon encountering an air channel, the dissolved-phase benzene that had partitioned into the vapor phase is removed from the soil profile with the effluent air flow. The action of mechanical dispersion, however, may have adverse effects; it may lead to the spreading of contamination into regions initially free of contamination.

Medium Air Flow Injection under Static Ground Water

For this test, the initial dissolved- and NAPL-phase pool had a benzene concentration of 800 mg/L in the upper region (Port S1), and the initial benzene concentration detected in the lower region (Port S2) was approximately 200 mg/L. Air was injected at a rate of 2,500 mL/min. The resulting zone of influence and air flow pattern was similar to the previous test performed at a low air flow rate (Fig. 3), but the greater air flow rate increased the air saturation and air channel density within the zone of influence.

Fig. 5 shows the changes in concentrations in the dissolved- and NAPL-phase pool (Ports S1 and S2) as air injection progressed. In the lower region (Port S2), the detected benzene concentration experienced continuous reductions with continued air injection. After 60 min of air injection, the concentration dropped from an initial value of 200 to 40 mg/L. After an additional 60 min of injection, the benzene concentration dropped below 10 mg/L. The upper contaminated region (Port S1) experienced similar benzene removal. After 60 min of air injection, benzene levels within this region dropped to approximately 300 mg/L. The concentration was further reduced to a level of 100 mg/L after 200 min of remediation time, and

further air injection resulted in undetectable benzene concentrations in this region. Fig. 5 also shows the overall removal of the initial benzene mass from the dissolved- and NAPL-phase pool with time. Approximately 65% of the initial benzene mass is removed within the first 60 min of air injection. Benzene removal continued at a high rate; 90% of the initial benzene mass is removed within the first 200 min of air injection, and the soil profile has nondetectable benzene concentrations after 700 min. Benzene removal occurred at a substantially faster rate than in the previous test that used a lower air injection rate, as shown in Figs. 4 and 5.

An increase in air flow increased the air channel density and air saturation within the zone of influence. The higher air saturation within the zone of influence in turn created a larger interfacial mass transfer area between the dissolved and NAPL phases and migrating air. This increased area allowed for increased rates of benzene partitioning into the vapor phase, enhancing the volatilization and removal rate. The increased volatilization affected both dissolved- and NAPL-phase benzene.

The increased air flow also increased the rate of trapped NAPL-phase removal. The increased air flow induced greater mechanical dispersion, leading to more efficient NAPL-phase benzene dissolution and subsequent transport and removal by breaking large NAPL ganglia into smaller droplets (Pankow et al. 1993). A greater volume of trapped NAPL-phase benzene was affected because its effect as a contaminant recharge source was eliminated. Sudden increases in benzene concentrations resulting from recharge were not detected. Additionally, as in the previous test, little if any spreading of the contaminant into the clean soil zones occurred, although a higher air injection rate was utilized.

High Air Flow Injection under Static Ground Water

To investigate the effect of high air flow rate, a test was conducted with a dissolved- and NAPL-phase pool consisting of approximately 700 mg/L benzene, using an air injection rate of 4,750 mL/min. A similar air flow pattern and zone of influence was observed in this test as compared to previous tests (Fig. 3), but the increased air flow led to an observed increase in the air saturation within the zone of influence due to increased air channel density.

Following the application of air injection, contaminant re-

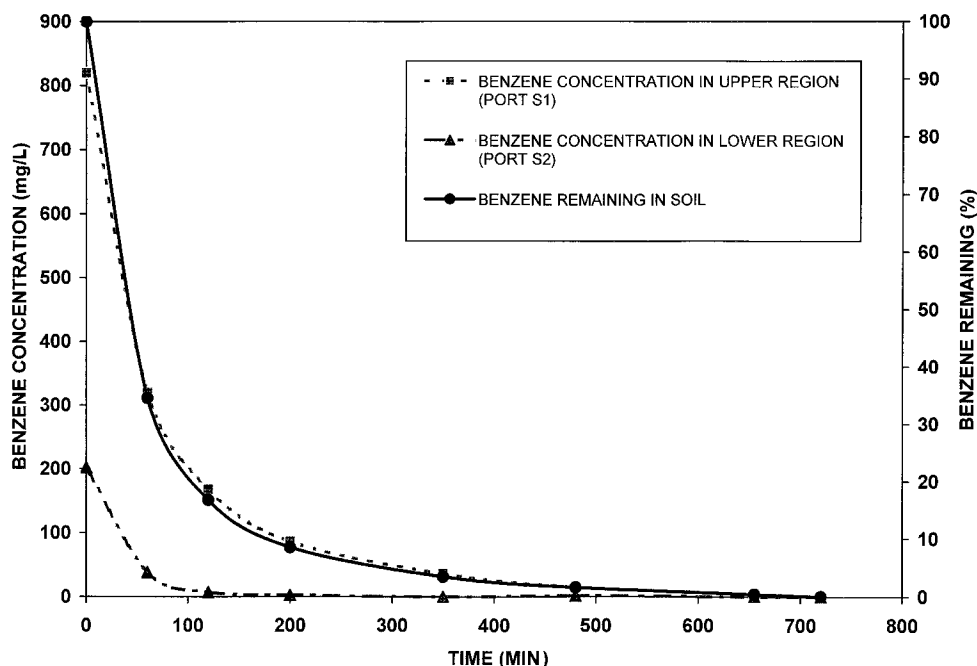


FIG. 5. Benzene Remaining versus Time; Air Flow Rate = 2,500 mL/min

removal similar to previous tests was observed, as shown in Fig. 6. However, the concentration in the lower region (Port S2) drops to 150 mg/L after 60 min of air injection, but this is followed by a concentration increase to 200 mg/L after an elapsed time of 180 min. Following this increase, most likely caused by contaminant recharge from trapped NAPL-phase contaminant, removal continues; a concentration of approximately 10 mg/L is detected after an elapsed time of 540 min. The upper contaminated region (Port S1) experiences continuous contaminant removal during the course of air injection. A benzene concentration of 225 mg/L is detected within this region after 60 min of air injection. Continued air injection leads to further removal at a high rate; the concentration is reduced to 100 mg/L after an additional hour of air injection,

and benzene concentrations are below the detection limit within the region after an elapsed time of 300 min.

Overall contaminant removal using a high rate of air injection was very similar to the behavior observed using a medium injection rate, as shown in Fig. 6. Almost 70% of the initial benzene mass was removed within the first 60 min of air injection. Approximately 15% of the initial benzene mass remains after 120 min of air injection, but an increase to 20% is observed 60 min later. This apparent increase reflects concentration fluctuations at the sampling ports and is not indicative of an actual benzene mass increase within the system. Further air injection reduces this to approximately 10% after 300 min of air injection, and approximately 99% of the initial benzene mass is removed after 780 min of air injection.

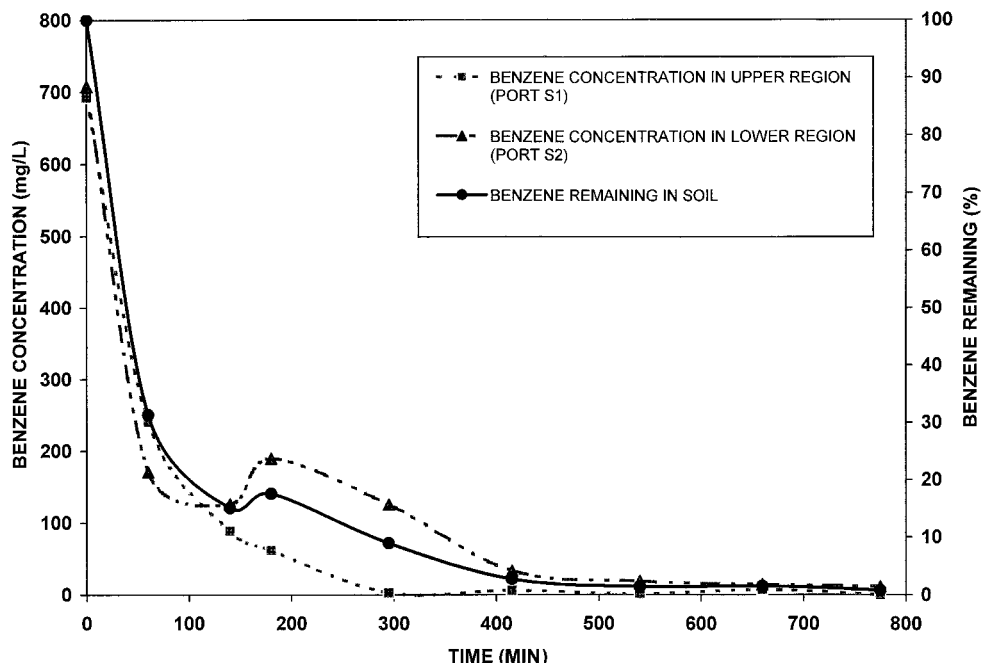


FIG. 6. Benzene Remaining versus Time; Air Flow Rate = 4,750 mL/min

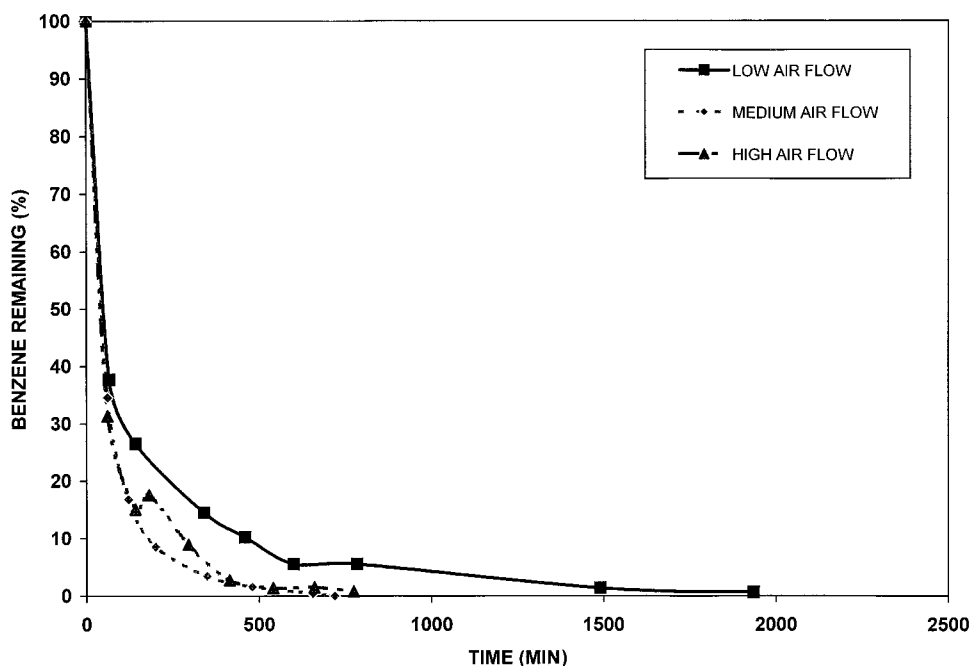


FIG. 7. Benzene Remaining versus Time; Various Air Injection Rates

Fig. 7 compares the overall removal using the three different air flow rates. The high air injection rate utilized during this test did not increase the rate of benzene removal significantly when compared to the medium air flow rate. Although a greater volumetric flow was traveling through the zone of influence, the rate of vapor-phase partitioning of the NAPL- and dissolved-phase benzene had reached a limit. At low air flow rates, increased air injection will increase the rate of vapor-phase partitioning. Eventually, however, a high injection rate is reached where further increases do not increase the rate of partitioning; less time for partitioning is available, and mass transfer resistance becomes an important factor. Therefore, increased air flow above the threshold rate will lead to unnecessary expenditures, with little or no increase in performance.

Utilization of a high air injection rate led to another noticeable phenomena; unlike the test utilizing a medium air injection rate, a notable increase in benzene concentration occurred, likely due to enhanced dissolution resulting from pore-water agitation. During this test, the high air injection rate created substantial mechanical dispersion, enhancing the partitioning of trapped NAPL-phase benzene into the dissolved phase, leading to removal through vapor-phase partitioning. Additionally, as in the previous tests of this study, spreading of benzene into clean zones was not observed.

Low Air Flow Injection under Ground-Water Flow

To study the effect of ground water on dissolved- and NAPL-phase pool removal using air sparging, a test was performed using an air flow rate of 2,500 mL/min and the same soil profile conditions described in the previous section; however, a ground-water flow with a gradient of 0.011 was applied to the dissolved- and NAPL-phase pool, contaminated soil profile. Upon injection of air at a rate of 2,500 mL/min, the resulting zone of influence and air flow pattern were observed to be similar to those seen in earlier tests utilizing a homogeneous coarse sand soil profile without ground-water flow (Fig. 3). The zone of influence completely enveloped the dissolved- and NAPL-phase pool.

Fig. 8 shows the benzene concentration within the pool region as well as regions downgradient from the pool as a function of time. As shown in this figure, an initial benzene con-

centration of 750 mg/L was detected in the lower region (Port S2). The concentration is reduced to below 10 mg/L after 65 min of air injection, and after 350 minutes of air injection, the remaining residual benzene concentration is not detectable. Minimal concentrations of benzene are detected downgradient from this region during the course of the test, as shown in Fig. 8, indicating that benzene migration out of the source region due to advective-dispersive transport induced by ground-water flow was not significant.

The benzene removal from the lower contaminant region differs from benzene removal from the upper contaminant region. The initial benzene concentration within the upper region (Port S1), as shown in Fig. 8, is 1,030 mg/L. This concentration is reduced to 230 mg/L after 65 min of air injection. With further air injection however, the rate of removal is reduced drastically, as evidenced by the attenuation of the contaminant versus time curve. Eventually, the remaining benzene contamination is removed with further air injection; a concentration of 25 mg/L is detected after 210 min of air injection, and benzene concentrations are nondetectable in the region after an elapsed time of 350 min.

The reduction of the benzene concentration within the upper region is not entirely controlled by vapor-phase partitioning and removal. Significant benzene concentrations are detected downgradient from the upper contaminant region as a result of advective-dispersive contaminant transport induced by ground-water flow. The region directly adjacent to the outflow water reservoir (Port D1) experienced significant benzene contamination as a result of this migration; as shown in Fig. 8, the region was initially contaminant-free, but after an elapsed time of 65 min, a benzene concentration of 125 mg/L was detected. With increased elapsed time, the concentration in this region is reduced slowly to 100 and 50 mg/L after 140 and 210 min of air injection, respectively. However, because very little, if any, of the injected air passes through this region, concentration reduction is the result of further migration downgradient with the ground-water flow. The rate of removal from the regions downgradient of the zone of influence is much less than the removal of contamination within the zone of influence, indicating that vapor-phase partitioning into the injected air is more efficient than removal/migration through ground-water-induced advective-dispersive mass transport.

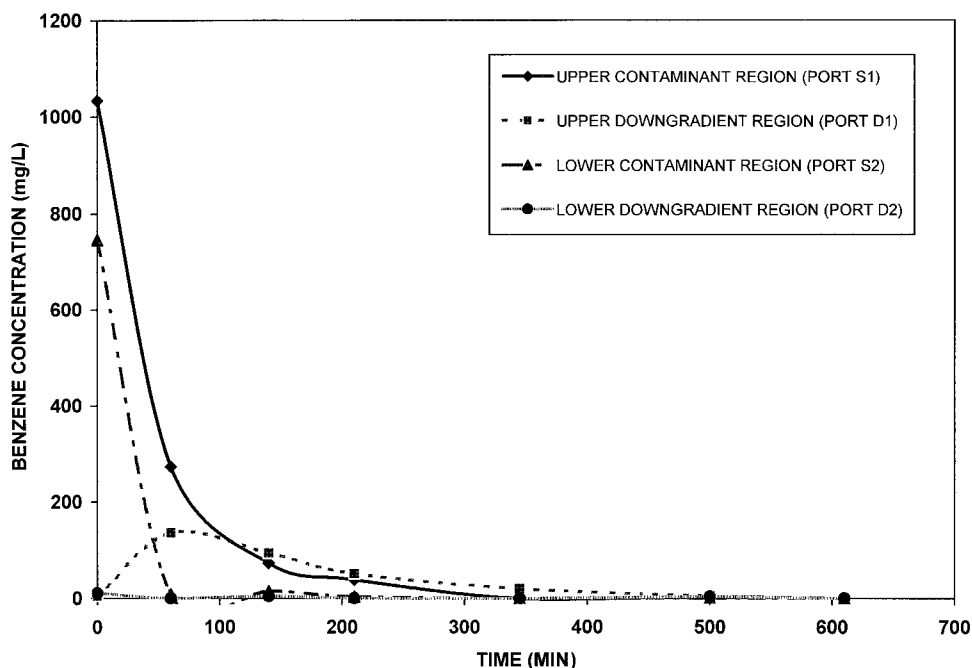


FIG. 8. Benzene Concentration versus Time; Air Injection Rate = 2,500 mL/min; Ground-Water Flow

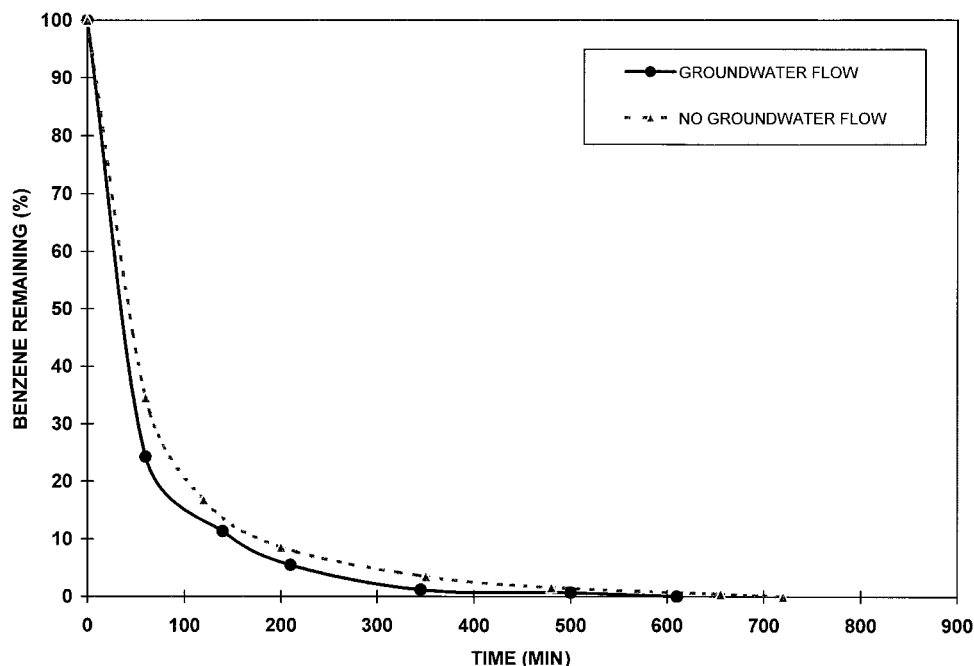


FIG. 9. Benzene Remaining versus Time; Air Injection Rate = 2,500 mL/min; Different Ground-Water Flow Conditions

The overall benzene mass removal versus time for an air injection rate of 2,500 mL/min subjected to both a static ground-water condition and ground-water flow is shown in Fig. 9. Approximately 75% of the initial benzene mass is removed after 60 min of air injection. This compares to 65% removal in the previous test using the same air injection rate but with a static ground-water condition. The apparent increased removal is attributed to spreading of benzene into downgradient regions due to ground-water flow as well as increased volatilization resulting from enhanced mixing in the pool zone.

The contaminant removal occurs within the zone of influence as a result of partitioning into the injected air. The injected air creates a large mass transfer interface area across which dissolved- and NAPL-phase benzene partitions into the vapor phase, allowing for efficient removal. Also, the injected air creates turbulence in the ground water within the zone of influence, inducing mechanical dispersion. The NAPL-phase contaminant partitions into the dissolved phase and migrates toward the air/water interface for removal.

A portion of the trapped NAPL- and dissolved-phase benzene may exist in immobile form and rely upon diffusion to reach mobile water or injected air. Because molecular diffusion constants of volatile organic contaminants in the aqueous phase are very small, diffusion out of immobile water or away from NAPL ganglia through a quiescent boundary layer of appreciable thickness to mobile ground water is slow and becomes a rate-limiting factor (Wilson et al. 1994). Partitioning of NAPL to the aqueous phase increases with increased ground-water velocity, but a limit is reached beyond which no further increases are realized (Miller et al. 1990). Additionally, NAPL ganglia size is an important factor; dissolution of small ganglia approaches a state of equilibrium with passing ground water, but increases in ganglia size result in a departure from nonequilibrium dissolution (Powers et al. 1991; Voudrias and Yeh 1994). If NAPL pools exist, diffusive transport controls; dissolved concentrations of volatile organic contaminants within passing ground water decrease with increased flow due to decreased contact time (Voudrias and Yeh 1994).

A second phenomenon that is created by air injection is a reduction in relative hydraulic conductivity due to increased air saturation. The ground water thus has a longer residence

time within the zone of influence, increasing benzene vapor-phase partitioning removal and reducing advection-induced migration by flowing water.

The low air injection rate used during this test, however, did not eliminate downgradient advective-dispersive benzene transport resulting from ground-water flow. As described earlier, substantial benzene spreading occurred within the regions downgradient from the upper initial contaminant region. This effect, however, is not seen downgradient from the lower contaminant region. Because the lower initial contaminant zone is closer to the point of injection, it is subjected to a higher density of air flow resulting in lower hydraulic conductivity, enhanced mechanical dispersion and dissolution, and a greater volatilization rate. The air flow within the upper contaminant zone is less dense, resulting in lower air saturation than within the lower contaminant zone. Less extensive volatilization and greater hydraulic conductivity resulted in significant spreading of benzene into downgradient regions.

High Air Flow Injection under Ground-Water Flow

To investigate how an increased air injection rate affects NAPL-phase contaminant removal and migration, an additional test was performed using an air injection rate of 4,750 mL/min. When air was injected into the soil profile, the air flow pattern and zone of influence was very similar to that observed in the previous low air flow injection test. However, the additional air flow led to a higher air saturation and greater air channel density within the zone of influence. Also, as in the previous test, the zone of influence completely enveloped the initial contaminant zone.

The contaminant concentrations in the pool as well as regions downgradient from the pool are shown in Fig. 10. As in the previous test, the initial contamination mass is confined to two regions directly above the injection point—an upper region (Port S1) and a lower region (Port S2). The initial benzene concentration detected in the lower region (Port S2) was approximately 560 mg/L. After 70 min of air injection, this concentration had dropped to 15 mg/L. After an elapsed time of 160 min, benzene was not detected within the region. Furthermore, regions downgradient from the lower contaminated regions experienced very little contamination due to benzene

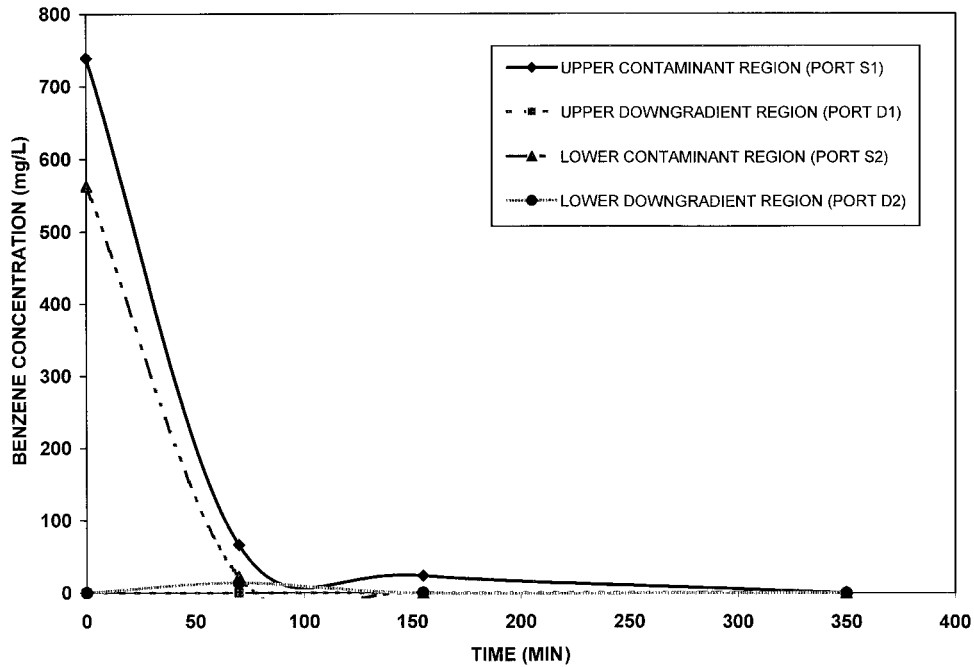


FIG. 10. Benzene Concentration versus Time; Air Injection Rate = 4,750 mL/min; Ground-Water Flow

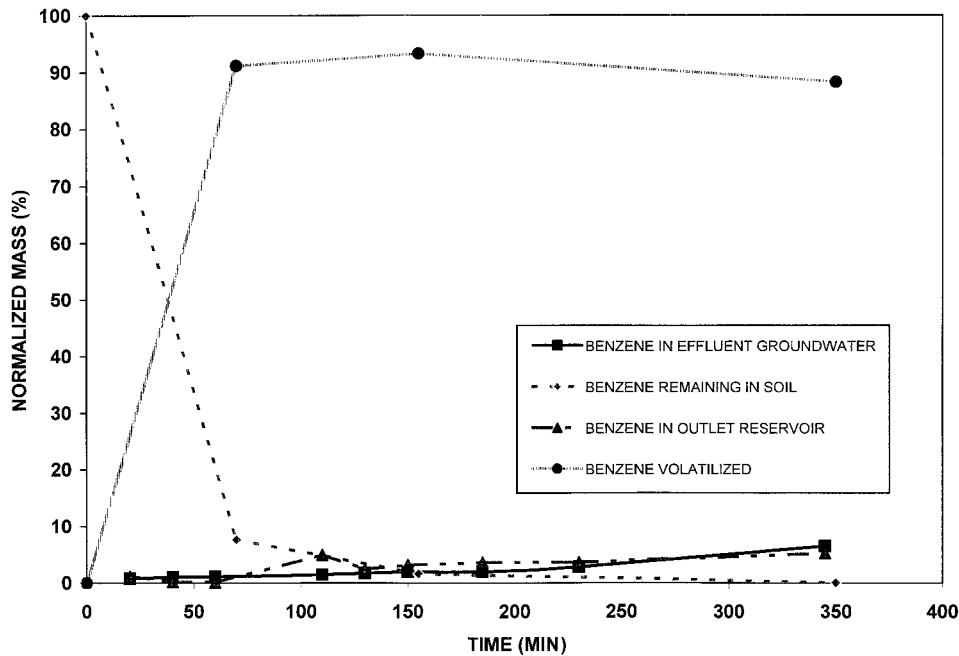


FIG. 11. Mass of Benzene Remaining versus Benzene Removed; Air Injection Rate = 4,750 mL/min with Ground-Water Flow

infiltration; as shown in Fig. 10, the highest detected concentration was approximately 15 mg/L after 70 min of air injection.

Very similar removal behavior is detected in the upper initial contaminant region (Port S1). The initial benzene concentration, approximately 740 mg/L, was reduced to approximately 70 mg/L after 70 min of air injection. Efficient removal due to vapor-phase partitioning continued until benzene concentrations were nondetectable within the region after an elapsed time of 350 min. Additionally, in contrast to the previous test, benzene was not detected at any time in regions downgradient from the initial upper contaminant region, as shown in Fig. 10. The higher air flow effectively reduced or eliminated spreading of contaminant in this region.

Fig. 11 shows the overall benzene mass removal versus the

benzene remaining within the profile. As shown, nearly 90% of the initial benzene mass is removed within the first 70 min of air injection. This rate of removal is substantially greater than mass removal at an air injection rate of 2,500 mL/min for conditions with and without ground-water flow (Fig. 9). After 160 min of air injection, 99% of the initial benzene mass had been removed, and the entire soil profile contained nondetectable levels of benzene after 350 min. The fast removal is the result of increased vapor-phase partitioning. Additionally, as shown in Fig. 11, approximately 6% of the initial benzene mass migrated out of the soil profile due to ground-water flow-induced advective dispersive transport. Over 90% of the initial benzene mass was removed from the soil profile due to volatilization.

Fig. 11 illustrates the significant effect of increased air in-

jection within the zone of influence. The resulting higher air saturation greatly enhances the mass transfer/transport mechanisms necessary for vapor-phase partitioning. The greater air flow increased the interfacial mass transfer area, allowing more efficient NAPL- and dissolved-phase partitioning of benzene into the vapor phase. The increased interface area led to rapid volatilization of a substantial portion of the initial benzene mass within the zone of influence. Additionally, the combination of the ground-water flow and the increased air flow greatly increased the effects of both mechanical dispersion and dissolution of NAPL-phase benzene. This quickly mobilized NAPL-phase benzene trapped within soil pores, greatly expediting total contaminant removal. Although the increased air flow enhanced the effectiveness of contaminant removal within the zone of influence, it also further reduced the relative hydraulic conductivity. Because the hydraulic conductivity was reduced, subsequent benzene migration due to advective mass transport was reduced greatly.

PRACTICAL IMPLICATIONS

The results of this study offer several important implications for the use of air sparging to remediate LNAPL pools. First, it has been shown that dissolved- and NAPL-phase pools can be readily removed using air sparging. Removal of NAPL-phase contaminant differs from the removal of dissolved-phase contamination. Injected air induces NAPL removal through enhancement of several mass transfer/transport mechanisms, namely mechanical dispersion, dissolution, and diffusion. Additionally, partitioning of NAPL-phase contaminant into the vapor phase readily occurs through volatilization, greatly enhancing removal.

When treating NAPL-phase contamination, caution must be exercised during monitoring of subsurface dissolved-phase contaminant concentrations. Trapped NAPL-phase contaminant can act as a source for further ground-water contamination even after mobile-phase ground water has been remediated. Therefore, during monitoring, sudden increases in concentration as a result of contaminant recharge from these sources should be expected. To treat trapped NAPL-phase contamination, increased air flow will enhance dissolution through increased mechanical dispersion as well as advective-dispersive transport, thereby improving removal efficiency. Increased air flow will increase the air saturation within the zone of influence, yielding more efficient removal. However, if air is injected at too high of a rate, phenomena that may prohibit effective remediation may occur, including soil fracturing, excessive advective-dispersive transport and possible off-site contaminant migration, and unnecessary expense resulting from equipment requirements and treatment of excessive volumes of effluent vapors.

Ground-water flow at a contaminated site can lead to off-site migration due to advective-dispersive transport. However, the use of air sparging to intercept a migrating contaminant plume can minimize or prevent migration by reducing the relative hydraulic conductivity within the zone of influence. Although it was shown that ground-water flow has little influence on the size and shape of the zone of influence of a sparge well, air injection will slow the flow of ground water through the zone of influence and ultimately reduce or eliminate advective-dispersive contaminant mass transport. Too high of an injection rate, however, may become problematic; if the relative hydraulic conductivity becomes too low within the zone of influence, ground water may follow a preferential flow path that would circumvent the zone of influence, preventing treatment. Therefore, an injection rate must be chosen to provide an acceptable rate of removal but prevent ground-water flow from circumventing the treatment zone.

CONCLUSIONS

This investigation was performed to study the removal of dissolved- and NAPL-phase benzene pools using air sparging. Two different ground-water flow scenarios were investigated—a static ground-water condition and a ground-water flow condition. All tests were performed using a homogeneous coarse sand layer. Several air injection rates were tested. The following conclusions may be drawn from this study:

- Dissolved- and NAPL-phase pools can be effectively removed through the use of air sparging. The application of air sparging will increase the rate of dissolution and dissolved-phase partitioning of NAPL-phase contamination. The mobile dissolved-phase contamination can partition into the vapor phase, expediting removal. Additionally, air sparging enhances mechanical dispersion and diffusion, inducing advective-dispersive and diffusive transport and allowing trapped NAPL-phase contamination to be removed.
- Increased air flow increased the rate of NAPL-phase contaminant removal. This occurs because additional air flow increased the interfacial mass transfer area through which NAPL-phase contaminant may partition into the vapor phase. Additional air flow enhanced the mass transfer/transport mechanisms, but a limit is reached where additional increases in the rate of air injection do not yield faster contaminant removal.
- During the application of air sparging to treat NAPL-phase contamination, trapped contamination will often serve as a contamination source for surrounding ground water. This causes concentrations to increase in pore water that has already been remediated. To effectively remediate a contaminated site, trapped contamination must be removed. Additionally, although advective-dispersive mass transport is an important removal mechanism when remediating dissolved-phase contamination, it did not appear to affect NAPL-phase contaminant removal. This may be due to the distribution of the contaminant; mobile NAPL- and aqueous-phase benzene easily partitioned into the vapor phase, but contaminant away from migrating air is often trapped, reducing its mobility and susceptibility to off-site migration.
- Injected air prevents advective-dispersive transport of NAPL- and dissolved-phase benzene with ground-water flow by reducing the hydraulic conductivity within the zone of influence. Because ground-water flow can mobilize and transport NAPL contamination, the use of air sparging can help prevent NAPL contaminant mobilization and flow out of the zone of influence. Increased air injection increased the rate of benzene removal by increasing the effect of the resulting mass transfer/transport mechanisms, dominating ground-water-induced advective mass transport and reducing ground-water flow. However, too high of an air injection rate may reduce hydraulic conductivity to a point where ground water will circumvent the zone of influence. Additionally, if air injection is too low, the air saturation will be too low to prevent ground-water flow through the zone of influence, resulting in substantial off-site migration. Therefore, the air injection rate must be selected to yield the desired remedial performance.

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