

Remediation of DNAPL source zones in groundwater using air sparging

Krishna R. Reddy and Luesgald Tekola

Abstract

Air sparging has shown to be a promising remediation technique for the treatment of saturated soils and groundwater contaminated by volatile organic compounds (VOCs). These compounds include non-aqueous phase liquids (NAPLs) that are typically classified by their density with respect to water; light NAPLs, or LNAPLs, are less dense, and dense NAPLs, or DNAPLs, are denser than water. Although air sparging is promising, the remedial efficiency of the process may vary considerably depending on the subsurface conditions that exist at the site and the system variables that are used. Source zones of free-phase (pure liquid) DNAPL may be particularly difficult to remediate, since the contaminant tends to form small globules that become trapped within the soil matrix. The present investigation was performed to evaluate and compare the spatial effects of different air injection rates on the remediation of DNAPL source zones, and to determine the effect of groundwater flow on the removal of DNAPL source zones during air injection. Five laboratory experiments were conducted using a two-dimensional (2-D) physical aquifer simulation apparatus containing homogeneous sand that was artificially contaminated with a DNAPL. The first three tests each used a progressively higher rate of air injection without groundwater flow, while the last two tests were performed using two different rates of air injection with groundwater flow, due to an identical 0.01 hydraulic gradient. The results showed that DNAPL source zones were effectively removed by air sparging, because the injected air increased volatilisation, dissolution and diffusion. Compared to the tests with lower airflow, the increased rate of airflow substantially enhanced removal because the additional air provided a greater interfacial area for DNAPL mass transfer. Using air sparging under groundwater flow conditions also resulted in an increased rate of contaminant removal, but this was partially due to undesirable off-site lateral contaminant migration, which occurred due to groundwater flow. Consequently, when groundwater flow was occurring, it was beneficial to use a higher airflow rate for two main reasons: (1) because the greater amount of air saturation provides faster removal, and (2) because the greater air saturation reduces the hydraulic conductivity of the sand, thereby hindering groundwater flow and lateral contaminant migration.

Key words: air sparging, DNAPLs, groundwater, laboratory, mass transfer, remediation, sand, volatilisation

INTRODUCTION

Non-aqueous phase liquids (NAPLs) have polluted the

soils and groundwater at numerous sites as a result of accidental spills or improper disposal practices. These contaminants include volatile organic compounds (VOCs) such as gasoline and its BTEX (benzene, toluene, ethylbenzene, and xylene) constituents, as well as chlorinated solvents such as trichloroethylene (TCE) and tetrachloroethylene (PCE). Within the subsurface, NAPL contaminants commonly bind with the soil, particularly soils with high organic contents, or become trapped in the soil matrix. These contaminants may exist as a free-phase (pure) liquid, as a dissolved-phase in the groundwater solution, and/or as a vapour-phase (Davis 1997). Generally, NAPLs are divided into two

Received February 2004; accepted April 2004

Authors

Krishna R. Reddy, Associate Professor, University of Illinois at Chicago, Department of Civil & Materials Engineering, 842 West Taylor Street, Chicago, Illinois 60607, USA. Tel. 312-996-4755. Fax 312-996-2426. Email: kreddy@uic.edu

Luesgald Tekola, Graduate Research Assistant, University of Illinois at Chicago, Department of Civil & Materials Engineering, 842 West Taylor Street, Chicago, Illinois 60607, USA

broad categories based on their density relative to water; light NAPLs, or LNAPLs, are less dense than water, whereas dense NAPLs, or DNAPLs, are denser than water. Thus, in the subsurface environment, LNAPLs tend to spread on the surface of the water table, and DNAPLs have a tendency to migrate toward the bottom of the aquifer.

Air sparging has proven to be an effective *in situ* remediation technique for treating NAPLs (particularly VOCs) that have contaminated saturated soils and groundwater (Marley *et al.* 1992; Johnson *et al.* 1993; Leonard and Brown 1994; Semer and Reddy 1998; Reddy and Adams 1999; Adams and Reddy 2000). In a conventional air sparging field system, compressed gas, usually air, is delivered to a manifold that apporions the gas flow to an array of injection wells. The gas travels into the subsurface via the injection wells to a depth below the region of contamination, and, since the gas is buoyant, it rises upward through the contaminated zone toward the ground surface. As the gas migrates through the NAPL zone, it removes the contaminants from the soil or groundwater, because the VOCs partition into the vapour phase and are transported upward with the buoyant gas toward the surface. The region of soil that is impacted by the injected air is known as the zone of influence (ZOI), and this region is largely a function of the soil permeability. Air sparging also facilitates contaminant removal by increasing the dissolved oxygen content of the subsurface and groundwater, which enhances aerobic biodegradation. Most air sparging systems are integrated with a soil vapour extraction (SVE) system that creates a vacuum near the surface to assist in capturing the contaminant-laden air as it rises to the unsaturated soil zone (vadose zone). After the contaminated air is extracted into the SVE system, it is treated using conventional air purifying methods, such as carbon filters and/or combustion, and then the clean air can be released to the atmosphere.

Contaminant transport primarily occurs due to three mechanisms, which are *advection*, *dispersion*, and/or *diffusion*. *Advection* describes the movement of the contaminant due to a pressure gradient, and, in the subsurface, the mass flux is proportional to the flow velocity, contaminant concentration, and the effective porosity of the media (Fetter 1999). *Dispersion* is the scattering, spreading, and/or mixing of the contaminant as a result of variations in micro-scale flow velocities. It should be noted that when a contaminant is flowing in a horizontal direction, the amount of dispersion could be quite different in the concurrent (longitudinal) direction compared to a direction that is perpendicular (transverse) to the direction of flow. Lastly, *diffusion* refers to the migration of the contaminant in response

to a concentration gradient. As a result of diffusion, contaminants migrate from regions of high concentration to regions of low concentration.

The partitioning of a contaminant from the dissolved- or free-phase to the vapour-phase (volatilisation) is the dominant contaminant removal process for air sparging (Johnson 1998). Free-phase NAPL contamination usually exists as small globules, which are easily trapped in soil pore spaces, so contaminant transport of free-phase NAPL is often limited. However, if these free-phase globules interact with air channels, removal can be rapid, because NAPLs will readily volatilise from the free-phase directly to the vapour-phase. Alternatively, with time, free-phase NAPL globules might dissolve and disperse into the groundwater, and, in a dissolved-phase, the contamination is more susceptible to transport but somewhat less volatile (Marley *et al.* 1992). At equilibrium, Henry's law relates the partial pressure of a compound in the vapour (gas) phase to its concentration in the aqueous-phase as follows:

$$P_a = C_{\text{water}} H_C$$

where P_a is the partial pressure of the compound in the gas-phase [atm], C_{water} is the concentration of the compound in the aqueous-phase [mol/m³], and H_C is the Henry's law constant [atm·m³/mol]. Henry's law shows that if different compounds have the same aqueous-phase concentration (C_{water}), the compound with the higher H_C value will result in a larger percentage of the contaminant partitioning to the vapour phase. However, it is important to note that due to the rapid movement of air through the contaminated zone, the gas- and aqueous-phase concentrations of the compound generally do not reach equilibrium during air sparging, so Henry's law constants only provide an indication of the amount of contaminant partitioning that will occur.

Air sparging has been employed at numerous field sites, and field trial studies have shown that the remedial performance varies considerably depending on the subsurface conditions that exist at the site and the system variables that are used (Ardito and Billings 1990; Marley *et al.* 1992; Leonard and Brown 1994; Lundegard and LaBrecque 1995; Bruell *et al.* 1997). The variations in remedial efficiency suggest that additional information and analysis is required to optimise the design of air sparging systems. In particular, it is important to investigate the effects of site-specific conditions, such as different soil types and contaminant properties and the presence of subsurface heterogeneities, as well as the effects of system variables, such as air-injection flow rate and pressure, pulsed air-injection, well spacing, and well depth, on contaminant fate and transport. Previous investigations have examined

the behaviour and effects of airflow patterns (Ji *et al.* 1993; Zumwalt *et al.* 1997; Semer *et al.* 1998; Reddy and Adams 2001) and the physico-chemical processes that affect contaminant removal (McKay and Acomb 1996; Rutherford and Johnson 1996; Braida and Ong 1997; Johnson *et al.* 1997; Semer and Reddy 1998; Johnson 1998). Furthermore, several studies have conducted mathematical modelling to assess and predict contaminant removal when using the air sparging process under different subsurface conditions (Sellers and Schreiber 1992; Ahlfeld *et al.* 1994; Wilson *et al.* 1994; Reddy *et al.* 1995; McCray and Falta 1997). Many of these previous investigations employed controlled laboratory testing using physical models, and these laboratory experiments were useful for describing airflow patterns, evaluating contaminant fate and transport, and for developing and validating numerical models.

Although previous air sparging studies have greatly contributed to improving the knowledge and design of air sparging systems, additional research is needed to further optimise the process and delineate the effects of various subsurface conditions and system parameters. In recent laboratory testing using physical models, it was concluded that air sparging was effective for the removal of dissolved- or free-phase LNAPL (benzene) or DNAPL (TCE) from homogeneous coarse sand (Adams and Reddy 1999; Adams and Reddy 2000). From these investigations, it was observed that the removal of dissolved-phase LNAPL and DNAPL was similar, and increased airflow corresponded to increased removal up to a threshold rate of airflow, after which further increases in airflow did not yield greater removal. The removal of free-phase NAPL was more difficult to analyse because NAPL globules became trapped in the soil matrix and non-uniform contaminant transport occurred, but, generally, the studies showed that increasing the airflow rate greatly enhanced removal. Furthermore, Adams and Reddy (2000) reported that when groundwater flow was occurring, air sparging reduced the migration of LNAPL out of the ZOI along with the groundwater, since the upward movement of air reduced the hydraulic conductivity and hindered groundwater advection through the contaminated zone.

The previous study by Adams and Reddy (2000) on the removal of dissolved- and free-phase LNAPL (benzene) was performed using a two-dimensional (2-D) laboratory aquifer simulation apparatus to assess spatially dependent variables. However, the previously described study on the removal of DNAPL (TCE) was conducted using a one-dimensional (1-D) column apparatus (Adams and Reddy 1999). These 1-D column tests were informative but somewhat deficient, because the spatial effects and the effect of groundwater flow could not be evaluated or compared to the

results of the 2-D LNAPL tests. Thus, the specific objectives of this present study were to evaluate and compare the spatial effects of air injection rate on the remediation of DNAPL source zones, and to determine the effect of groundwater flow on the removal of DNAPL source zones during air injection. The same 2-D apparatus and homogeneous sand soil used in the previous study by Adams and Reddy (2000) was used in the present study to allow a direct comparison of the use of air sparging for LNAPL versus DNAPL source zones.

EXPERIMENTAL PROGRAMME

Aquifer simulation setup

The 2-D aquifer simulation test apparatus that was used is shown in Figure 1, and an identical test apparatus was used in previous air sparging tests (Adams and Reddy 2000; Reddy and Adams 2001). The tank was made of Plexiglas[®] and measured 111 cm in length, 72 cm in height, and 10 cm in width. The extent of contaminant adsorption to the Plexiglas[®] was determined to be negligible (Reddy and Adams 2001). The interior of the tank consists of three compartments; a soil chamber measuring 91 cm in length was centred within the tank and this chamber was bordered by two groundwater reservoirs, each measuring 10 cm in length. The head level in each groundwater reservoir was adjustable to allow the creation of a hydraulic gradient across the central soil chamber. The groundwater reservoirs were separated from the central 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. One side of the tank had twenty sampling ports arranged in four rows and five columns, each protruding into the central soil chamber. The ports allow for the sampling of pore water from the soil profile throughout the course of a test.

Materials

As in the previous tests with LNAPL (Adams and Reddy 2000), uniform coarse sand obtained from US Silica Company (US Silica designation 20/40 fraction) was used as the test soil for this research. The sand was poorly graded with a $D_{10} = 0.43$ mm and $D_{50} = 0.55$ mm. The hydraulic conductivity of sand was 0.05 cm/sec and the porosity under the test conditions had a value of 0.4. trichloroethylene (TCE) (Fisher Scientific) was chosen as the representative DNAPL because it is one of the most commonly used chlorinated solvents, and it has been encountered at numerous contaminated sites. TCE (CAS # = 79-01-6, C_2HCl_3 , MW = 131.37) has a Henry's law constant of approximately

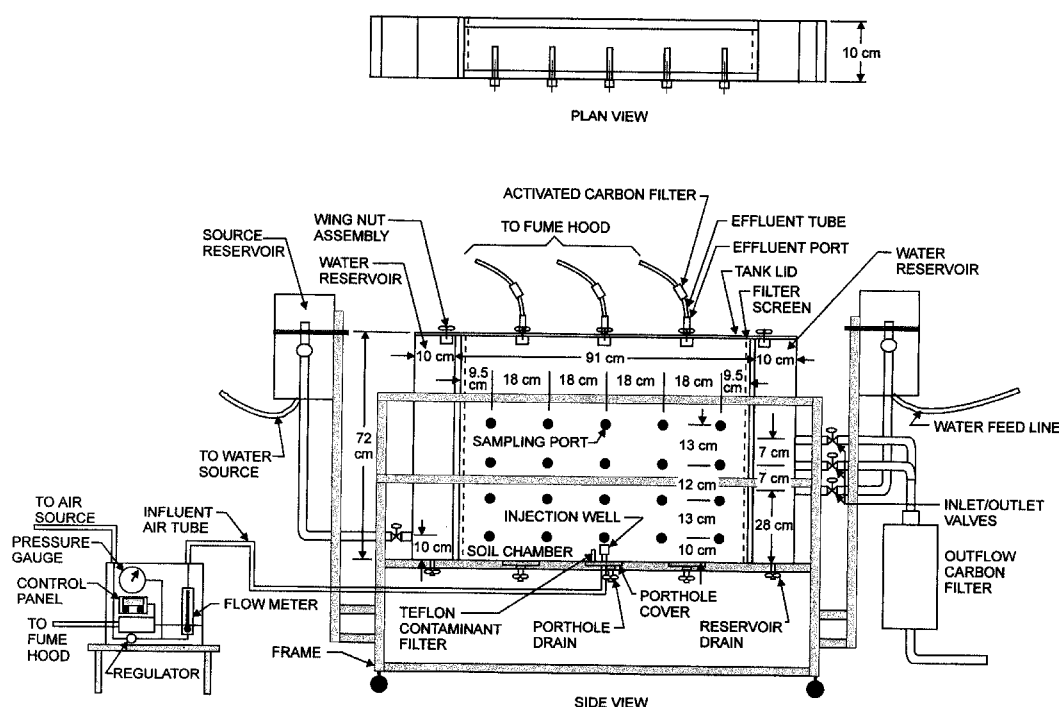


FIGURE 1. SCHEMATIC OF TWO-DIMENSIONAL AQUIFER SIMULATION TEST SETUP

0.11 bar-mol/kg at 25°C (NIST), a specific gravity of 1.47, and a vapour pressure of 58 mm Hg at 20°C (Fisher Scientific).

Testing programme

Table 1 shows the testing programme for this study. All the tests were performed using homogeneous coarse sand and TCE. The first three tests were performed under a static groundwater condition, and each test used a different air injection rate of 2225 mL/min, 4750 mL/min, or 7156 mL/min. The three air injection rates

were introduced under a pressure of 6.9 kPa. In addition, two tests were conducted at an airflow rate of 2225 mL/min or 7156 mL/min with induced groundwater flow using a hydraulic gradient of 0.01.

Testing procedure

The soil profile was formed in the same manner that was used in previous investigations utilising the identical 2-D test apparatus (Adams and Reddy 2000; Reddy and Adams 2001). In all of the tests, coarse sand was placed through the top of the 2-D test apparatus using a

Table 1. Testing programme for TCE DNAPL source zone study

Porous media	Contaminant	Airflow rate (mL/min)	Air pressure (kPa)	Hydraulic gradient
Coarse sand	TCE	2225	6.9	0
Coarse sand	TCE	4750	6.9	0
Coarse sand	TCE	7150	6.9	0
Coarse sand	TCE	2225	6.9	0.01
Coarse sand	TCE	7150	6.9	0.01

consistent drop height. The mass and volume of the placed sand were recorded to calculate the density and porosity. A high concentration/free-phase TCE solution was prepared by injecting 2.6 mL of pure TCE into 940 mL of deionised water. The TCE solution was prepared within a sealed bottle and headspace was minimised to restrict contaminant losses due to volatilisation. The mixture was placed on a magnetic stirrer and mixed for approximately an hour.

After the soil placement was completed, approximately half of the soil profile was saturated with water by allowing the water to infiltrate the soil from the side water reservoirs, thereby forming a water table within soil profile (Figure 1). The contaminant mixture was then injected into the soil profile just above the water table through a slotted stainless-steel probe that was placed into the soil from the top of the tank. Once the contaminant zone was established, the remainder of the soil profile was saturated with water. The tank cover was fastened and sealed in place and effluent air tubes (Cole-Parmer C-Flex tubing) fitted with ORBO tube activated carbon filters were connected to the tank cover. Once the cover was in place, the pore water sampling was performed to define the initial contaminant concentration profile, and air injection was commenced at the predetermined airflow rate and pressure. A control panel consisting of a pressure regulator, pressure gauge, and flow meter was used to certify the

proper air pressure and flow throughout testing. The ORBO tube filters allowed the effluent to be monitored during each test to verify contaminant removal and ensure quality control.

Pore water sampling and subsequent gas chromatographic (GC) analysis was performed prior to the commencement of air injection as well as at regular intervals throughout the test duration, to evaluate remedial progress. The pore water sampling procedure first consisted of extracting 100 μL from each sampling port using a gas-tight syringe. Each 100 μL sample was then immediately diluted into 5 mL of deionised water and loaded into a Tekmar 2016 Purge and Trap Autosampler for automatic injection into the GC. The GC chemical analysis was conducted using a Hewlett Packard 6890 GC with a Supelco 60/80 Carboxapack column and a flame ionisation detector (FID). Adams and Reddy (1999) provide further details about the particular GC run that was used. To assure accuracy, the GC was calibrated before each test, using an external standard (TCE); blank samples were injected between sampling procedures to verify no contaminant carryover occurred; and duplicate samples were analysed to confirm proper measurement. Selected duplicate tests were also performed to assure experimental reproducibility.

As mentioned earlier, in addition to pore water sampling, the contaminant removed into the vapour phase was evaluated at different time intervals by replacing

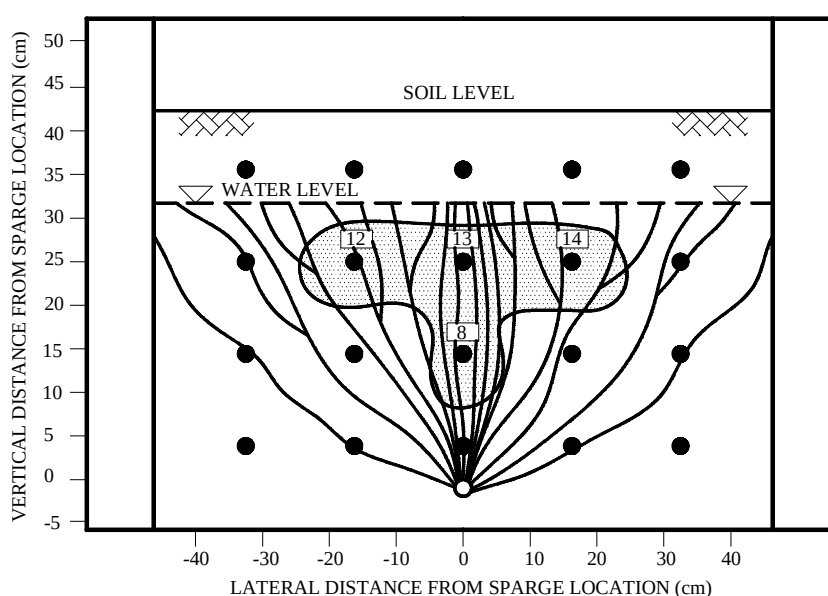
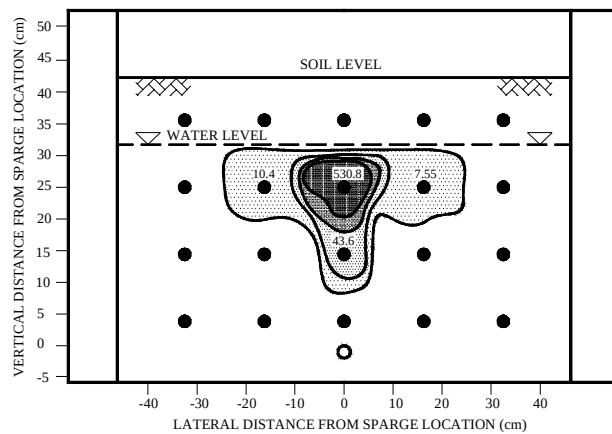
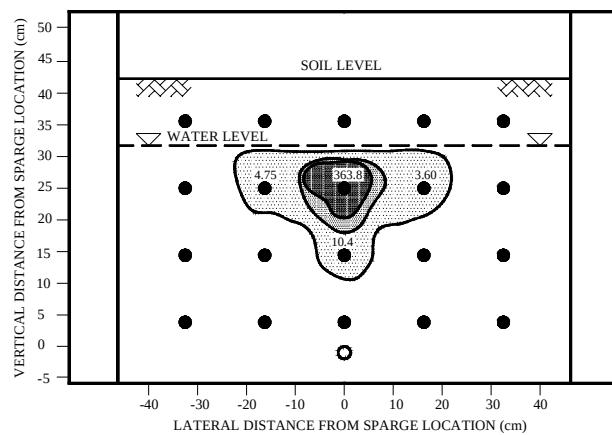


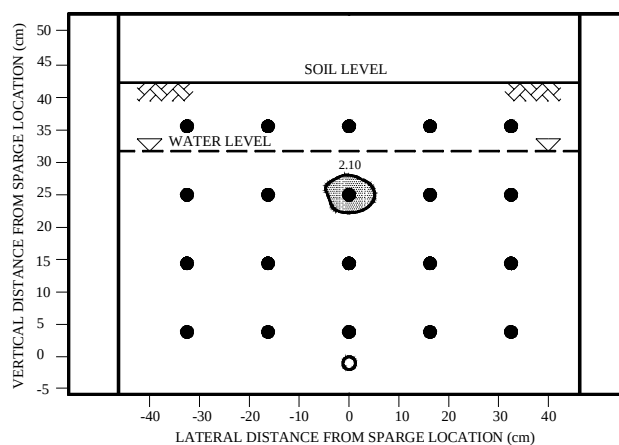
FIGURE 2. INITIAL TCE NAPL POOL ZONE AND AIR DISTRIBUTION UNDER AIRFLOW RATE = 2225 ML/MIN (SHOWS PORT NUMBERS WITHIN THE SOURCE ZONE)



(a) $t = 0$ minutes



(b) $t = 60$ minutes



(c) $t = 3030$ minutes

FIGURE 3. SPATIAL DISTRIBUTION OF TCE DURING AIR INJECTION UNDER AIRFLOW RATE = 2225 ML/MIN: (A) $T = 0$ MINUTES; (B) $T = 60$ MINUTES; AND (C) $T = 3030$ MINUTES

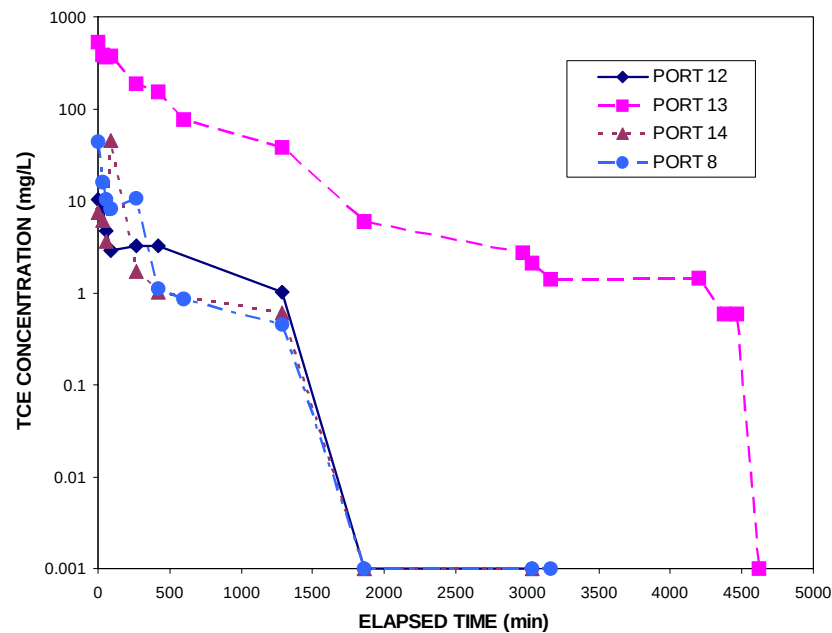


FIGURE 4. MEASURED TCE CONCENTRATION WITHIN THE SOURCE ZONE DURING AIR INJECTION UNDER AIRFLOW RATE = 2225 ML/MIN

the ORBO tubes. After each ORBO tube was removed, the tube was broken and the charcoal was placed into a 40 mL glass vial along with carbon disulphide (Fisher Scientific, ACS grade). The vials were then shaken for 24 hours to extract the TCE from the charcoal into the liquid phase, and a sample of the extractant liquid was removed for injection into the GC using a gas-tight syringe.

RESULTS AND ANALYSIS

Air sparging under static groundwater conditions

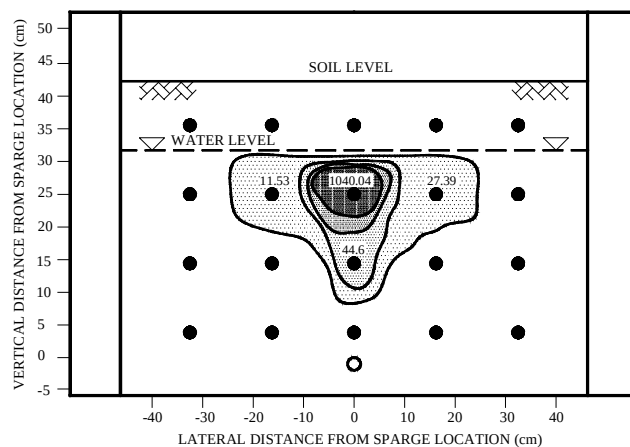
Experiment with airflow rate = 2225 mL/min

Figure 2 shows the airflow pattern and ZOI for the test using the 2225 mL/min airflow rate, and, by observing Figures 2 and 3 (a), it can be seen that the ZOI completely enveloped the zone of contamination. Initially, before the commencement of air sparging, the concentrations of TCE in the upper (Port 13) and lower (Port 8) regions of the contaminated zone were 531 and 44 mg/L, respectively (Figure 3 (a)). After 60 minutes of air injection, Figure 3 (b) shows that the TCE concentration in these regions dropped substantially. In the upper region, the concentration dropped from 531 to 364 mg/L, which is about a 30% reduction, and, in the lower region, the concentration dropped from 44 to 10 mg/L, which is nearly an 80% reduction. Figure 3 (c) shows that after 3030 minutes of air injection, the TCE

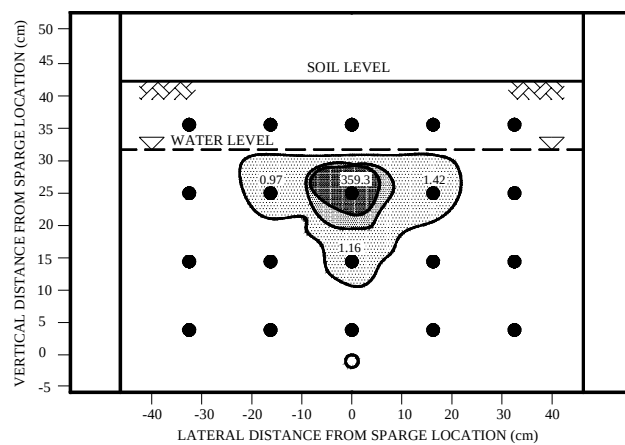
was almost completely removed from the soil profile.

Figure 4 illustrates that the TCE concentration in the upper region (Port 13) of the contaminated zone decreased more slowly than in the lower region (Port 8), but the initial concentration in the upper region was over twelve times higher. In addition, it should be noted that the lower region was closer to the point of air injection. As observed in Figure 2, as the air channels migrate vertically through the soil profile, lateral migration also occurs, and this is because the horizontal permeability was probably much greater than the vertical permeability (Nyer and Suthersan 1993). Although this airflow pattern is beneficial because it results in an increased ZOI with increasing height from the point of air injection, the air channel density per unit volume of soil decreases with height. Thus, the greater volume of air per unit volume of soil in the lower regions generally results in a bottom to top pattern of contaminant removal, which was also observed in previous studies conducted with LNAPL contamination (Adams and Reddy 2000; Reddy and Adams 2001).

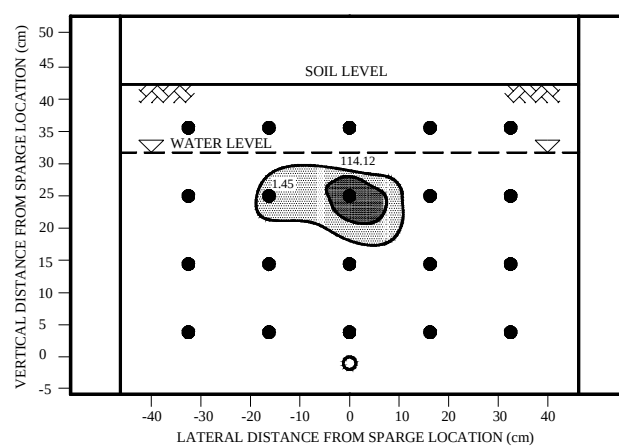
As observed in Figure 4, after an elapsed time of approximately 400 minutes, the concentration of TCE slightly increased in the lower region (Port 8) of the contaminated zone, and there are several reasons why this minor fluctuation in the TCE concentration may have occurred. One reason is that some of the free-



(a) $t = 0$ minutes



(b) $t = 180$ minutes



(c) $t = 420$ minutes

FIGURE 5. SPATIAL DISTRIBUTION OF TCE DURING AIR INJECTION UNDER AIRFLOW RATE = 4750 ML/MIN: (A) $T = 0$ MINUTES; (B) $T = 180$ MINUTES; AND (C) $T = 420$ MINUTES

phase DNAPL globules from the initially injected mixture may have become trapped in the soil matrix, and, over time, these globules might have dissolved and seeped or diffused from the pore spaces into the groundwater, consequently rebounding the contaminant concentration. In addition, since TCE is denser than water, some downward DNAPL migration may have occurred from the upper region, but, as seen in Figures 3 (a), 3 (b), and 3 (c), the amount of downward migration appeared to be minimal. To a large extent, the upward airflow migration probably counteracted the tendency for the DNAPL to migrate downward. Another cause for fluctuating TCE concentration and downward contaminant migration from the upper region is diffusion, since the contaminant concentration in the upper region was substantially higher than in the lower region. Moreover, as discussed earlier, there was a greater volume of air per unit volume of soil travelling through the lower contaminant zone, which resulted in a higher rate of TCE removal. Thus, the concentration gradient between the upper and lower regions of the contaminated zone was increasing, and this probably resulted in a higher rate of diffusion.

It is important to note that the TCE concentration in the upper (Port 13) zone of contamination reduced

from about 531 to below 10 mg/L in less than 2000 minutes, but another 2500 minutes were required to lower the concentration further from 10 to below 1 mg/L (Figure 4). This behaviour illustrates the difficulty in removing low contaminant concentrations and shows that there was a persistent tailing effect in this test. Evidently, after the majority of the contamination had been removed during the early stages of testing through relatively fast contaminant transfer due to volatilisation, the removal of the remaining contamination was controlled by diffusion, which may be a very slow process, especially when the concentration gradient is small.

As stated earlier, Adams and Reddy (2000) previously performed a comparable air sparging study with the same 2-D apparatus and homogeneous sand. These investigators used a slightly higher airflow rate of 2500 mL/min to remove LNAPL (benzene), and the removal rate of LNAPL was much more rapid than that observed in the present study with DNAPL (TCE). The initial concentration of benzene (800 mg/L) was higher than the initial concentration of TCE (530 mg/L) in the upper region (Port 13), yet the removal time for benzene was relatively fast (around 700 minutes), whereas it was about 4500 minutes for TCE – over six times as long. Evidently, the chemical properties of benzene,

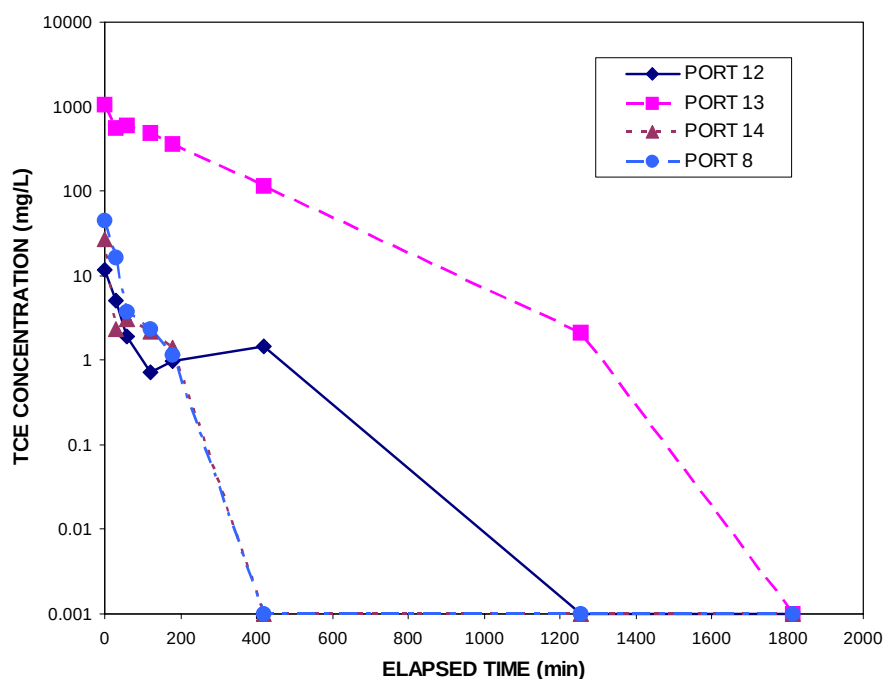


FIGURE 6. MEASURED TCE CONCENTRATION WITHIN THE SOURCE ZONE DURING AIR INJECTION UNDER AIRFLOW RATE = 4750 ML/MIN

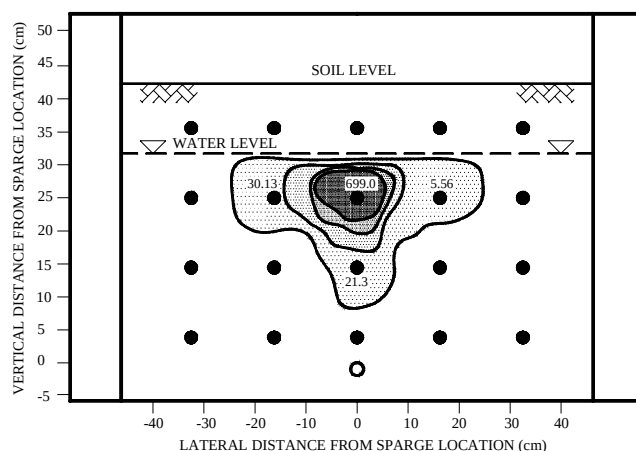
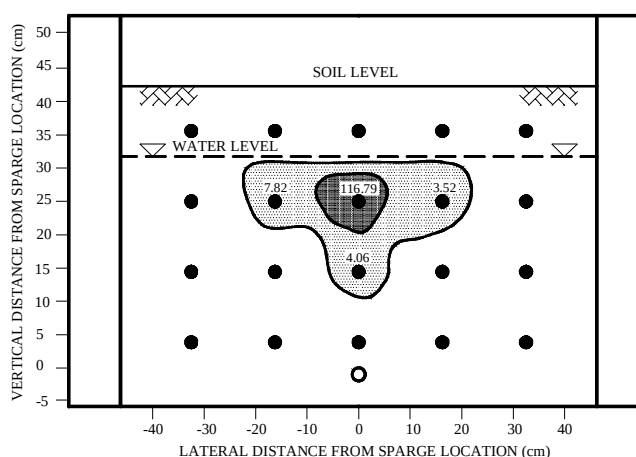
(a) $t = 0$ minutes(b) $t = 60$ minutes

FIGURE 7. SPATIAL DISTRIBUTION OF TCE DURING AIR INJECTION UNDER AIRFLOW RATE = 7150 ML/MIN: (A) $T = 0$ MINUTES; AND (B) $T = 60$ MINUTES

such as its higher volatility and solubility, facilitated much faster contaminant removal compared to TCE, and these results suggest that the type of contaminant greatly affects the remedial efficiency of air sparging.

Experiment with airflow rate = 4750 mL/min

The airflow pattern and ZOI for the test with the 4750 mL/min rate was very similar to the previous test with the 2225 mL/min rate (Figure 2), but the higher airflow rate produced slightly more air channels and had greater air saturation per unit volume of soil. Figure 5 (a) shows that the upper (Port 13) and lower (Port 8)

regions of the zone of contamination had initial TCE concentrations of 1040 and 45 mg/L, respectively. After 180 minutes, Figure 5 (b) shows that the TCE concentration dropped considerably from 1040 to 359 mg/L (65% reduction) in the upper region and from 45 to 1 mg/L (98% reduction) in the lower region. As observed earlier with the test performed with the 2225 mL/min rate, the rapid removal of TCE from the lower region is attributed to the conical airflow pattern and the greater volume of air per unit volume of soil at the lower depths (Figure 2). Figure 5 (c) shows that after an additional 240 minutes of air injection, the TCE con-

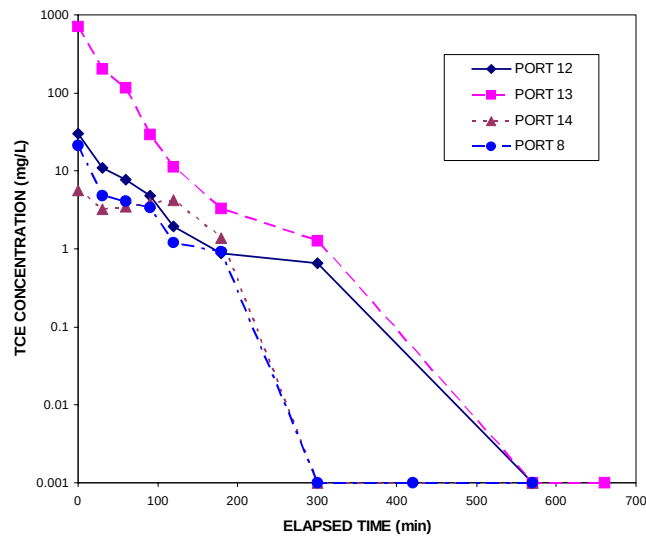


FIGURE 8. MEASURED TCE CONCENTRATION WITHIN THE SOURCE ZONE DURING AIR INJECTION UNDER AIRFLOW RATE = 7150 ML/MIN

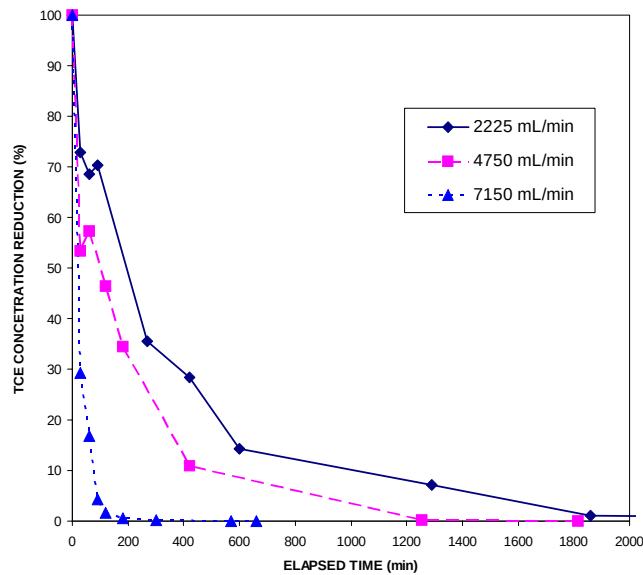


FIGURE 9. EFFECT OF AIRFLOW RATE ON THE TCE MASS REMOVAL FROM THE SOURCE ZONE

centration dropped from 359 to 114 mg/L in the upper region (Port 13), which was a 68% reduction. This indicates that the TCE removal rate was reasonably consistent with respect to the percentage of contaminant removed from the upper region per unit time. However, the actual drop in TCE concentration that occurred in

this region during the initial 180 minutes (a drop of 681 mg/L) was much greater than in the following 240 minutes (a drop of 245 mg/L). The majority of the contaminant was probably removed during the initial stages of air injection by volatilisation, but the remaining low concentration of DNAPL globules that were trapped in

the soil matrix away from any air channel were most likely removed through dissolution and diffusion, which was a much slower process. This behaviour can be observed in Figure 6, where nearly an additional 1400 minutes were required to reduce the TCE concentration in the upper region (Port 13) from 114 mg/L to a negligible value.

Compared to the lower 2225 mL/min airflow rate, the higher 4750 mL/min airflow rate was clearly advantageous for TCE removal. As seen in Figures 3 (a) and 5 (a), the upper region (Port 13) in the lower airflow test had an initial TCE concentration of 530 mg/L, which was nearly half the concentration of the same region in the higher airflow test (1040 mg/L). However, even though the test with the lower airflow rate had a much lower initial TCE concentration, it needed about 4500 minutes to accomplish TCE removal, whereas the test with the higher airflow rate, which had nearly twice the initial TCE concentration, achieved TCE removal in around 1800 minutes, which was less than half the time. These results conflict with the results from the comparable 2-D air sparging study conducted by Adams and Reddy (2000), because these investigators reported that the 4750 mL/min airflow rate did not significantly increase the rate of LNAPL (benzene) removal compared to the lower airflow rate of 2500 mL/min. Adams and Reddy (2000) stated that a threshold rate of airflow was reached where further increasing the rate of airflow would not reduce the removal time. This indicates that it is important to consider the type of compound when choosing the rate of airflow, because a high airflow rate may be beneficial for removing DNAPL contamination but an unnecessary expense for removing LNAPL compounds. Although the higher airflow rate did not significantly reduce the removal time for benzene compared to the lower airflow rate, the removal time (700 minutes) was still substantially less than the removal time for TCE (1800 minutes) at the same high airflow rate of 4750 mL/min. As hypothesised earlier, it seems that the chemical properties of benzene, such as its higher volatility and solubility, facilitated much faster contaminant removal compared to TCE.

Experiment with airflow rate = 7156 mL/min

The airflow pattern and ZOI for the test with the 7156 mL/min rate was similar to the pattern observed in the earlier tests (Figure 2), but this very high airflow rate resulted in many more air channels and extremely high air saturation per unit volume of soil. In this test, the TCE concentration in the upper region of the contaminant source zone was initially 699 mg/L (Figure 7 (a)), but the concentration in this region was substantially reduced to 117 mg/L (83% reduction) in the first 60

minutes of air injection (Figure 7 (b)). As shown in Figure 8, this test using the very high airflow rate behaved like the earlier experiments with lower airflows, because the majority of the TCE was removed during the initial stages of testing, due to volatilisation, and much more time was required to remove the remaining contaminant through dissolution and diffusion. However, in this test with the very high airflow rate, the contaminant concentration at Port 13 was reduced from 117 mg/L to a negligible value in less than 600 minutes, whereas in the earlier test using the airflow rate of 4750 mL/min, over twice the amount of time (1400 minutes) was required to reduce the concentration from 114 mg/L to a negligible value. This indicates that higher airflow rates are advantageous for dissolution and slower contaminant transport mechanisms such as diffusion. Figure 9 shows that compared to the earlier tests using lower rates of airflow, the very high airflow rate of 7156 mL/min was tremendously beneficial for TCE removal and rapidly lowered the contaminant concentration within the soil profile. Clearly, high airflow rates greatly enhance DNAPL removal, and a threshold airflow rate was not observed, even though the very high airflow rate of 7156 mL/min was about 1.5 times the 4750 mL/min threshold airflow rate reported for LNAPL contamination in Adams and Reddy (2000).

Air sparging under groundwater flow condition

Experiment with airflow rate = 2225 mL/min

Figure 10 (a) shows the initial TCE concentrations in the contaminated zone before air injection was commenced, and, compared to the identical conducted earlier with static groundwater, these results show that some downgradient lateral advection and dispersion of the contaminant source zone occurred before the start of the test due to the flow of groundwater. Upon injection of air at the flow rate of 2225 mL/min, the observed airflow pattern and ZOI was similar to those seen in the previous tests without groundwater flow (Figure 2), so, apparently, the induced groundwater flow with a 0.01 hydraulic gradient did not exhibit any noticeable effect on the size and/or shape of the ZOI. Figure 10 (b) shows that after only 30 minutes of air injection, the TCE concentrations in the soil had been reduced substantially, and, since a relatively high TCE concentration remained at Port 13 after 60 minutes in an identical test conducted earlier with static groundwater conditions (Figure 3 (b)), the rapid removal in this test was mainly attributed to the advection and dispersion of TCE with the flow of groundwater. Although air sparging probably contributed to some contaminant removal, these results indicate that a large portion of the TCE underwent lateral migration due to the presence of groundwater flow. As seen in Figure 10

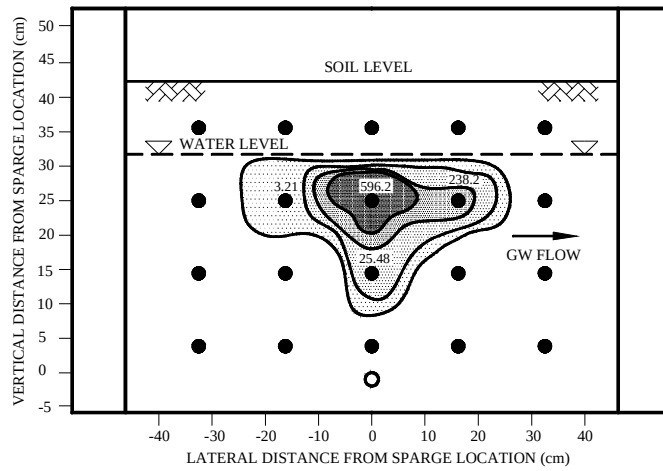
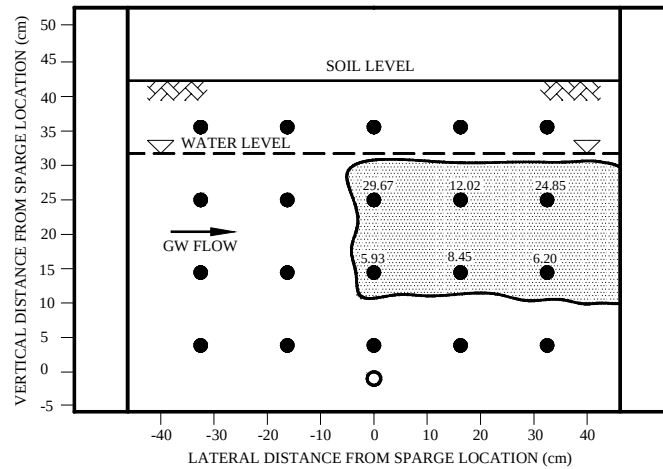
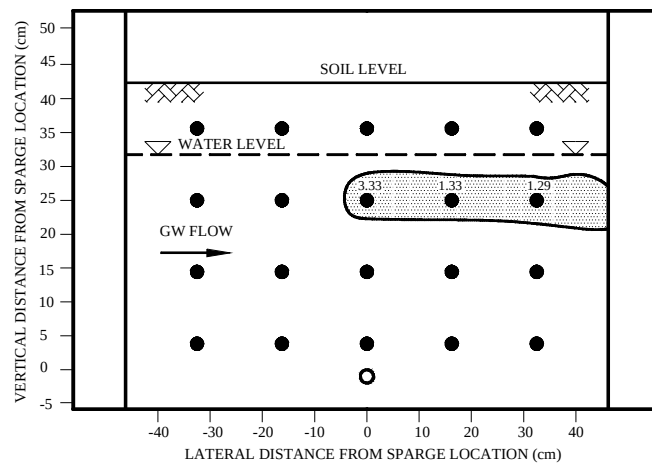
(a) $t = 0$ minutes(b) $t = 30$ minutes(c) $t = 560$ minutes

FIGURE 10. SPATIAL DISTRIBUTION OF TCE DURING AIR INJECTION UNDER AIRFLOW RATE = 2225 ML/MIN AND GROUNDWATER FLOW CONDITION: (A) $T = 0$ MINUTES; (B) $T = 30$ MINUTES; AND (C) $T = 560$ MINUTES

(c), even with air sparging combined with groundwater flow, a relatively long amount of time was required to remove the comparatively low TCE concentrations observed after 30 minutes in Figure 10 (b). Figure 11 illustrates that TCE concentrations were still detected for approximately another 2000 minutes beyond the initial 30-minute stage when most of the contamination was removed, so, it seems that groundwater flow may not improve the rate of diffusion.

Experiment with airflow rate = 7156 mL/min

Compared to the same test conducted earlier with static groundwater, prior to the commencement of air injection, it is evident that the flow of groundwater caused the lateral advection and dispersion of the TCE source zone downgradient (Figure 12 (a)). After air was injected into the soil profile, the airflow pattern and ZOI appeared similar to those observed in the previous tests (Figure 2); however, as seen in the identical test without groundwater flow, the additional airflow rate in this test produced greater air channel density and higher air saturation throughout the ZOI. Figure 12 (b) shows that after just 30 minutes, the TCE concentrations reduced substantially, and, although the initial contaminant concentration also dropped quickly in the identical test without groundwater flow (Figure 7 (b)) due to the very high airflow rate, these results suggest that a large amount of TCE advection and dispersion occurred due to the flow of groundwater. As seen in Figure 13, the combination of the high airflow rate coupled with the groundwater flow caused the TCE to be removed from this experiment in just over 400 minutes, which was less time than in any of the other previous

tests.

The two experiments that were conducted with groundwater flow (Figures 10 (a,b,c) and 12 (a,b)) show that it was advantageous to use the higher airflow rate for two main reasons; (1) because the greater amount of air saturation allowed faster removal, which was observed earlier in the identical test conducted without groundwater flow, and (2) because the greater air saturation reduced the hydraulic conductivity of the sand, thereby hindering groundwater flow and lateral contaminant migration. Since the upward airflow creates air channels and displaces water in the soil pore spaces, there are fewer flow paths available for groundwater movement, resulting in lower hydraulic conductivity. It is critical to understand that lateral downgradient contaminant transport from the soil profile as a result of groundwater flow is extremely undesirable, because this produces off-site contaminant migration that can severely impact public health and the environment. Therefore, it is of the utmost importance to select a high airflow rate for the remediation of DNAPL source zones when there is considerable groundwater flow.

CONCLUSIONS

DNAPL source zones can be effectively removed through the use of air sparging, because the injected air increases the volatilisation, dissolution and diffusion of DNAPL contamination. The experiments that provided a higher rate of airflow substantially enhanced removal over the identical tests with lower airflow because the

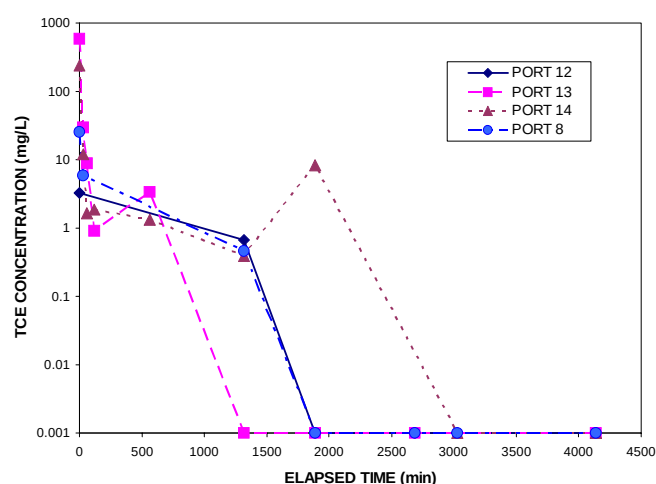
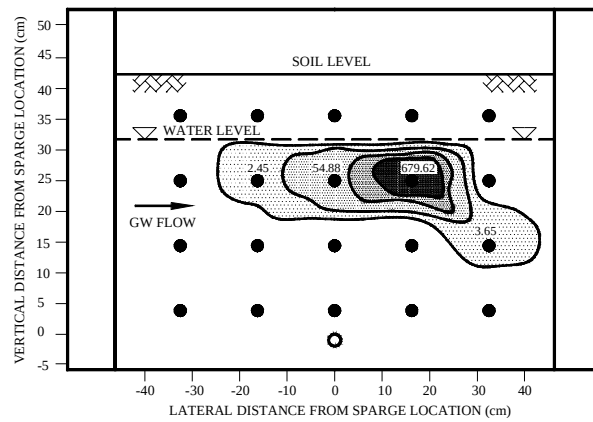
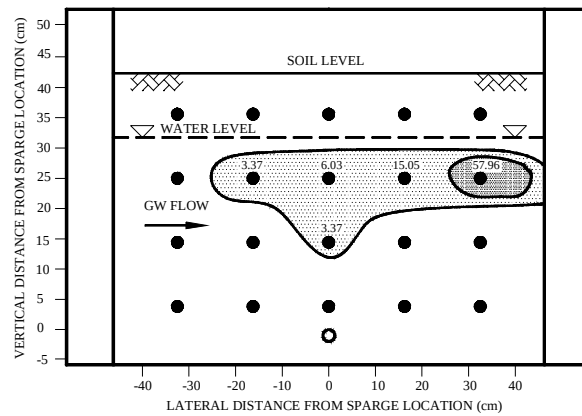


FIGURE 11. MEASURED TCE CONCENTRATION WITHIN THE SOURCE ZONE DURING AIR INJECTION UNDER AIRFLOW RATE = 2225 ML/MIN AND GROUNDWATER FLOW CONDITION



(a) $t = 0$ minutes



(b) $t = 30$ minutes

FIGURE 12. SPATIAL DISTRIBUTION OF TCE DURING AIR INJECTION UNDER AIRFLOW RATE = 7150 ML/MIN AND GROUNDWATER FLOW CONDITION: (A) $T = 0$ MINUTES; AND (B) $T = 30$ MINUTES

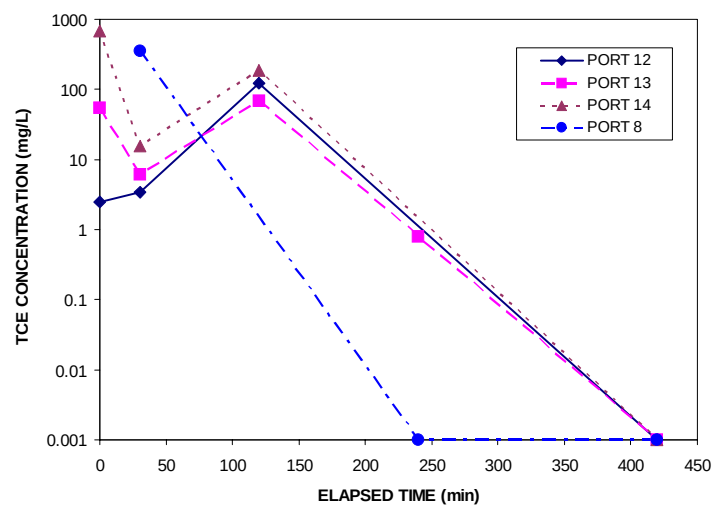


FIGURE 13. MEASURED TCE CONCENTRATION WITHIN THE SOURCE ZONE DURING AIR INJECTION UNDER AIRFLOW RATE = 7150 ML/MIN AND GROUNDWATER FLOW CONDITION

additional air provided a greater interfacial area for DNAPL mass transfer to occur. Using air sparging under groundwater flow conditions also increased the rate of contaminant removal, but undesirable off-site lateral contaminant migration occurred due to groundwater flow, which could be detrimental to public health and the environment. Consequently, when groundwater flow was occurring, it was beneficial to use a higher airflow rate for two main reasons: (1) because the greater amount of air saturation provides faster removal, and (2) because the greater air saturation reduces the hydraulic conductivity of the sand, thereby hindering groundwater flow and lateral contaminant migration.

REFERENCES

- Adams, J.A. and Reddy, K.R. (1999) Laboratory study of air sparging of TCE-contaminated saturated soils and ground water. *Ground Water Monitoring Review*, **19** (3), 182–190
- Adams, J.A. and Reddy, K.R. (2000) Removal of dissolved- and free-phase benzene pools from ground water using *in-situ* air sparging. *Journal of Environmental Engineering, ASCE*, **126** (8), 697–707
- Ahlfeld, D.P., Dahmani, A. and Ji, W. (1994) A conceptual model of field behavior of air sparging and its implications for application. *Ground Water Monitoring Review*, **14** (4), 132–139
- Ardito, C.P. and Billings, J.F. (1990) Alternative remediation strategies: the subsurface volatilization and ventilation system. In *Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration*. National Groundwater Association, Westerville, Ohio, 349–363
- Braida, W.J. and Ong, S.K. (1997) Factors affecting air sparging remediation technologies. In *Proceedings of the Fourth International Symposium on In-Situ and On-site Bioremediation*, **1**, 187–192. Battelle Press, Columbus, Ohio
- Bruell, C.J., Marley, M.C. and Hopkins, H.H. (1997) American Petroleum Institute air sparging database. *Journal of Soil Contamination*, **6** (2), 169–185
- Davis, E.L. (1997) How heat can enhance *in-situ* soil and aquifer remediation: important chemical properties and guidance on choosing the appropriate technique. EPA/540/S-97/502. Washington, DC
- Fetter, C.W. (1999) *Contaminant Hydrology*. Prentice Hall, Upper Saddle River, NJ
- Ji, W., Dahmani, A., Ahlfeld, D.P., Lin, J.D. and Hill III, E. (1993) Laboratory study of air sparging: air flow visualization. *Ground Water Monitoring Review*, **13** (4), 115–126
- Johnson, P.C. (1998) Assessment of the contributions of volatilization and biodegradation to *in-situ* air sparging performance. *Environmental Science and Technology*, **32** (1), 276–281
- Johnson, P.C., Das, A., Johnson, R.L., Leeson, A., McWhorter, D. and Hinchey, R.E. (1997) Effects of IAS process changes on the removal of immiscible-phase hydrocarbons. In *Proceedings of the Fourth International Symposium on In-situ and On-site Bioremediation*, **1**, 135–140. Battelle Press, Columbus, Ohio
- Johnson, R.L., Johnson, P.C., McWhorter, D.B., Hinchey, R.E. and Goodman, I. (1993) An overview of *in-situ* air sparging. *Ground Water Monitoring Review*, **13** (4), 127–135
- Leonard, W.C. and Brown, R.A. (1994) Air sparging an optimal solution. In *Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Preventive, Detection, and Restoration*. National Groundwater Association, Westerville, Ohio, pp. 349–363
- Lundegard, P.D. and LaBrecque, D. (1995) Air sparging in a sandy aquifer (Florence, Oregon, USA): Actual and apparent radius of influence. *Journal of Contaminant Hydrology* **19** (1), 1–27
- Marley, M.C., Hazebrouck, D.J. and Walsh, M.T. (1992) The application of *in-situ* air sparging as an innovative soils and groundwater remediation technology. *Ground Water Monitoring Review*, **12** (2), 137–145
- McCray, J.E. and Falta, R.W. (1997) Numerical simulation of air sparging for remediation of NAPL contamination. *Ground Water*, **35** (1), 99–100
- McKay, D.J. and Acomb, L.J. (1996) Neutron moisture probe measurements of fluid displacement during *in-situ* air sparging. *Ground Water Monitoring Review*, **16** (4), 86–94
- Nyer, E.K. and Suthersan, S.S. (1993) Air sparging: savior of groundwater remediation or just blowing bubbles in the bathtub? *Ground Water Monitoring Review*, **13** (4), 87–91
- Reddy, K.R. and Adams, J.A. (1999) Laboratory study of air sparging of TCE contaminated saturated soils and ground water. *Ground Water Monitoring and Remediation*, **12**, 182–190
- Reddy, K.R. and Adams, J.A. (2001) Effects of soil heterogeneity on airflow patterns and hydrocarbon removal during *in-situ* air sparging. *Journal of Geotechnical and Geoenvironmental Engineering*, **127** (3), 234–247
- Reddy, K.R., Zhou, J. and Kosgi, S. (1995) New model to simulate air sparging for groundwater remediation. In *Pro-*

ceedings of 5th WERC Development Conference, New Mexico State University, Las Cruces, New Mexico, pp. 299–308

Rutherford, K.W. and Johnson, P.C. (1996) Effects of process control changes on aquifer oxygenation rates during *in situ* air sparging in homogeneous aquifers. *Ground Water Monitoring Review*, **16** (4), 132–141

Sellers, K.L. and Schreiber, R.P. (1992) Air sparging model for predicting groundwater cleanup rate. In *Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration in Houston, Texas*, pp. 365–376. National Groundwater Association, Dublin, Ohio

Semer, R. and Reddy, K.R. (1998) Mechanisms controlling toluene removal from saturated soils during *in situ* air sparging. *Journal of Hazardous Materials*, **57** (1–3), 209–230

Semer, R., Adams, J.A. and Reddy, K.R. (1998) An experimental investigation of air flow patterns in saturated soils during air sparging. *Geotechnical and Geological Engineering Journal*, **16** (1), 59–75

Wilson, D.J., Gomez-Lahoz, C. and Rodriguez-Maroto, J.M. (1994) Groundwater cleanup by *in situ* air sparging, VIII: Effect of air channeling on dissolved volatile organic compounds removal efficiency. *Separation Science and Technology*, **29**(18), 2387–2418

Zumwalt, G.S., Krishna, A.P. and Nelson, J.D. (1997) Air distribution within a sparging cone of influence. In *Proceedings of the Fourth International Symposium on In-Situ and On-site Bioremediation*, **1**, 141–146. Battelle Press, Columbus, Ohio

