

Mechanisms controlling toluene removal from saturated soils during in situ air sparging

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Abstract

In situ air sparging is an effective method for removing volatile organic compounds from saturated soils and groundwater. Removal efficiency levels as high as 98% are often reported, and the remediation time is significantly less than that required for conventional pump and treat technology. However, predictions of the time required for contaminant mass removal by air sparging have been approximate at best due to a lack of understanding of the relative importance of the various mechanisms that are responsible for this contaminant removal. Volatilization is considered the most dominant mass transfer mechanism during the air sparging process. Dissolution, desorption and biodegradation are the other major mechanisms that determine the rate at which contaminants are partitioned into different phases or transformed into nonhazardous substances. Additionally, advection, dispersion and diffusion are the transport mechanisms that dictate the overall contaminant removal efficiency. This paper first describes these different mechanisms along with the factors that affect these mechanisms. Then, experimental data is presented for toluene removal from Ottawa sand and fine gravel by means of air sparging. The tests performed included batch tests to characterize the adsorption characteristics of toluene on the Ottawa sand, and air sparging column tests on both the sand and the gravel to provide information on the effects of soil type and injected air flow rate on the overall air sparging remedial efficiency. These test results are assessed in light of the mechanisms affecting contaminant removal during air sparging. © 1998 Elsevier Science B.V.

Keywords: Air sparging; Groundwater; Saturated soils; Remediation; Hydrocarbons; Mechanisms; Laboratory investigation

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1. Introduction

In situ air sparging (IAS) is a relatively new technology used for remediating saturated soils and groundwater which have been contaminated with nonaqueous phase liquids (NAPLs), and, in particular, volatile organic compounds (VOCs). IAS involves injecting pressurized air below the contaminant zone in the subsurface. The injected air then partitions the contaminants into the vapor phase and transports the contaminants to the unsaturated zone where the vapors are captured by extraction wells and subsequently treated aboveground [1]. The injected air may also enhance the biodegradation of the contaminants. Although air sparging has been in use for less than ten years, it is quickly replacing pump and treat technology as the treatment method of choice for remediating petroleum spill and leaking underground storage tank sites because of significant reduction in remedial time and lower costs.

Limited field pilot tests are usually conducted in order to determine the necessary spacing of the injection and extraction wells based upon the observed zone of influence of each test well. Other system parameters including the injection air flow rate and pressure, and the vacuum pressure in the extraction wells, are also determined based on these pilot test results as well as empirical considerations. These parameters are highly dependent on the specific site geology including the soil permeability and soil heterogeneity. The majority of literature that reviews air sparging field studies illustrates successful use of this method; however, the specific mechanisms that allow the air sparging process to be effective for remediating saturated soils and groundwater have not as of yet been evaluated [1].

The results from previous laboratory investigations on the air sparging process have helped to understand air flow patterns in saturated soils. Ji et al. [2] used different sized glass beads to simulate air flow patterns under various soil conditions. This research showed that injected air travels in the form of bubbles in highly porous soils such as gravel, whereas in less permeable soils such as sand, the injected air travels in the form of microchannels. The study also showed that the injected air does not penetrate soils with very low permeability, such as clay, unless extremely high pressure is initially used. This study also concluded that highly permeable soils (e.g. gravel) may be so permeable that the zone of influence in these soils is too small to use IAS as a viable remediation method. Semer and Reddy [3] also performed similar laboratory air sparging experiments, but used actual soils to assess the air flow patterns under different conditions. This study showed that the air flow patterns that develop during air sparging depend significantly on the soil type, groundwater flow conditions, injected air flow rate and pressure, and the applied vacuum pressure used for extraction.

To date, laboratory experiments specifically designed to investigate the contaminant removal mechanisms that occur during air sparging have not been reported. However, a number of other unrelated studies have been reported which examined the mechanisms of volatilization, dissolution, adsorption/desorption, biodegradation, advection, dispersion and diffusion in soil and/or water. This paper reviews these studies in relation to toluene which is the particular VOC selected for this study in order to assess the predominant contaminant transport and transformation processes which affect air sparging efficiency. The relative significance of these different mechanisms is evaluated on

the basis of laboratory air sparging column experiments conducted on two types of soil, Ottawa sand and fine gravel, that were contaminated with toluene. Batch tests were also performed to characterize the adsorption of toluene in Ottawa sand.

2. Review of mechanisms

An extensive literature review was conducted in order to examine the mechanisms that are responsible for the removal of contaminants during air sparging. Based on this review, contaminant removal during air sparging can be attributed to: (1) the mass transfer of VOCs from one phase to another, (2) the transformation of VOCs into nonhazardous substances, and (3) the transport of VOCs. The most important mass transfer mechanisms which occur during air sparging are volatilization, dissolution, and adsorption/desorption. The transformation of VOCs into nonhazardous substances occurs in the presence of microbes due to biodegradation. The advection, dispersion (mechanical dispersion), and diffusion (molecular diffusion) are the transport processes of VOCs. Because this study dealt with toluene as a typical VOC, these mechanisms are specifically addressed for toluene removal from saturated soils using air sparging.

2.1. Contaminant mass transfer or partitioning mechanisms

2.1.1. Volatilization

Volatilization is defined as the partitioning of the liquid phase compound to the vapor phase, and this is the most dominant mechanism that occurs during air sparging [4,5]. The air sparging process upsets the equilibrium between the gas and liquid phases by gas phase advection, which reduces the vapor phase concentration of the VOC. The resistance encountered when a VOC partitions from the liquid phase to the gas phase is often negligible. Hsieh et al. [6] experimentally determined that the ratio of gas phase to liquid phase mass transfer coefficients were in the range of 2.2–3.6 in a diffused aeration system as compared to 38–110 in a surface aeration system. Therefore, the resistance of the gas phase to partition into the liquid phase is insignificant for surface aeration systems, whereas this resistance is highly significant for diffused aeration systems. Because air sparging utilizes diffused aeration, the mass removal rate predictions for volatilization of VOCs during air sparging should take gas phase resistance into account.

The volatility of a specific contaminant is indicated by its vapor pressure and Henry's constant. A contaminant is considered strippable and, therefore, suitable for remediation by air sparging if it possesses a vapor pressure greater than 5 mm Hg and a Henry's constant greater than 10^{-5} atm m³/mol [7,8]. Toluene has a vapor pressure of 21 mm Hg and a Henry's constant in the 10^{-2} atm m³/mol range, and, therefore, it is easily volatilized for removal by air sparging. Other common VOCs such as benzene, ethylbenzene, and xylenes also possess similar characteristics as toluene and are also suitable for removal by air sparging.

Volatilization is governed by different laws depending upon whether the contaminant is dissolved in an organic solvent or dissolved in water. Raoult's Law governs in the unsaturated zone where the contaminant exists as a component in a mixed organic phase [9,10]. This law, which is valid for equilibrium conditions, states that the partial pressure of any particular contaminant vapor above a non-aqueous phase liquid (NAPL) is equivalent to the mole fraction of the contaminant in the NAPL multiplied by the compound's pure component vapor pressure:

$$P_i = P_{vp} X_i \quad (1)$$

where P_i = partial pressure of the contaminant (atm), P_{vp} = vapor pressure of the pure compound (atm), and X_i = molar fraction of contaminant i in mixture. The greater the vapor pressure of the contaminant, the more likely that the contaminant will exist in the gas phase. The amount of contaminant mass that can be removed by extraction wells in the unsaturated soil zone is calculated using Raoult's Law in conjunction with the ideal gas law and local equilibrium [9,10]. However, Raoult's Law together with local equilibrium conditions have been shown to be inadequate for predicting the quantity of mass removal when concentrations are low, when heterogeneities exist in flow patterns in the subsurface resulting in uneven weathering of the NAPL, or when there are mass transfer limitations from the aqueous or solid phase to the gas phase [10].

The distribution of VOC in the gas and liquid phases is determined by Henry's Law when the VOC is dissolved in water as in the saturated zone. Henry's law states that under equilibrium conditions, the partial pressure of a gas (i.e. volatile chemical) above water is proportional to the concentration of that chemical in the liquid:

$$P_g = H_c C_l \quad (2)$$

where P_g = partial pressure of the gas (atm), H_c = Henry's constant (atm m^3/mol), and C_l = concentration of chemical in the liquid (mol/ m^3). The higher the Henry's constant, the more likely that the contaminant will exist in the vapor phase at equilibrium. However, nonequilibrium conditions exist in systems which utilize diffused air, such as air sparging systems, because of the changes in contaminant concentrations in the vapor phase as the air rises through the soil. The Henry's constant of the contaminant helps to assess whether the injected air will be saturated with the chemical before it reaches the extraction wells. The greater the Henry's constant for the VOC, the greater amount of contaminant vapor that can be accepted by the rising air bubbles before saturation is reached. The Henry's constant of a particular chemical can be increased by elevating the temperature since vapor pressure is highly dependent on temperature. Although higher Henry's constants result in a greater proportion of the VOC in the gas phase, several researchers contend that increased Henry's constants do not cause significant decreases in overall remediation time because most volatilization of contaminants take place during the early stages of air sparging [11–13]. During the later stages of the air sparging process, the residual contamination which is not in direct contact with the injected air may not be conducive to volatilization. Nevertheless, knowing the volatilization rate will aid in determining the rate at which the bulk of the contamination can be removed.

2.1.2. Dissolution

The NAPLs dissolve partially in the groundwater depending on their aqueous solubilities. Dissolution into the groundwater will continue until equilibrium is established, resulting in a maximum concentration of the dissolved contaminants. The solubility of pure toluene in water is in the 515–540 mg/l range at 25°C [14–16]. Toluene is less soluble than benzene; however, it is more soluble than the other BTEX compounds (ethylbenzene or xylenes). Water table fluctuations may cause a NAPL which is floating on the water table to be displaced in the form of discrete ganglia or as lenses within the porous medium. The NAPL may be trapped due to air-NAPL and water-NAPL interfacial tensions; consequently, high contaminant concentrations in the capillary fringe can exist.

The dissolution of toluene into water occurs very slowly. Voudrias and Yeh [16] demonstrated based on laboratory tests that even under a high concentration gradient, the dissolution of toluene occurs slowly and occurs only to a limited extent. This study estimated that one liter of toluene occupying a 69 cm × 20 cm × 2 cm pool will dissolve in 8 and 12 years with average groundwater velocities of 60.9 and 28.2 cm/day, respectively, under a continuous groundwater pumping condition. Pulsed pumping, instead of continuous pumping, increased the mass removal by 20 percent per unit volume of water pumped and, therefore, the volume of wastewater that had to be treated decreased. However, the overall remediation time was higher for the pulsed pumping condition.

Malone et al. [17] contended that the assumption of equilibrium does not accurately predict dissolution rates. Another approach, documented by Hunt et al. [14], Powers et al. [18], and Borden and Kao [19] showed that nonequilibrium mass transfer models more accurately describe the dissolution rate. These models show extensive tailing in the dissolution process, where mass transfer decreases when the concentration becomes low. Powers et al. [18] made the tentative conclusion that nonequilibrium mass transfer between NAPLs and groundwater will influence organic compound concentrations for spills which are small in size, have high Darcy's velocities, low residual NAPL saturations, and large blob sizes often caused by heterogeneity in aquifers. The cleanup times and the volume of water predicted for treatment are several times greater when using the nonequilibrium assumption than when using the local equilibrium assumption.

Unger et al. [13] stated that while volatilization is the dominant process in the removal of NAPLs during the early stages of air sparging, the process becomes limited by dissolution at intermediate and later times. This hypothesis was tested by first modeling a decrease in volatility by a factor of two, and then simulating a decrease in solubility by a factor of two. A decrease in volatility caused only a marginal increase in the number of air and water pore volumes that needed to be remediated, while the decrease in solubility doubled the number of pore volumes of water that needed to be removed which caused a proportional increase in the remediation time.

Air sparging aids in the dissolution of VOCs in groundwater. If the water is quiescent, the concentration gradient will be greatest at the surface, and dissolution will be slow. However, if air is being injected into the subsurface, mixing is increased as indicated in the experiments performed by Voudrias and Yeh [16] where pulsed air mixing aided in mass removal. A synergistic effect occurs during air sparging because of

the combined effects of gas phase advective contaminant removal and liquid phase mixing.

2.1.3. Adsorption and desorption

The adsorption and desorption of a contaminant are important mechanisms to consider when quantifying the contaminant mass removal rates that result from the air sparging process. The organic contaminants can be adsorbed in a very thin layer to the exposed edges of clay, or they can be sorbed into a thin layer of naturally occurring organic matter on soil surfaces. Nonpolar molecules have stronger attraction to the soil organic matter than to the mineral surfaces. The adsorption of BTEX increases with the organic content in soils [20]. Toluene is more easily adsorbed than desorbed in organic-rich soils [20]. The ratio of the adsorption to the desorption partition coefficients is higher for soils that contain significant amounts of organic material. If the ratio of adsorption to desorption is unity or less, the medium has no retention capabilities which implies that the adsorption is reversible.

The amount of adsorption of an organic contaminant onto soil is more dependent on the organic content of the soil. The adsorption partition coefficient (K_p) is generally used to determine the amount of adsorption and is empirically related to the organic fraction in the soil (f_{oc}) and the normalized partition coefficient (K_{oc}) as follows:

$$K_p = K_{oc} f_{oc}. \quad (3)$$

The published values of K_{oc} are quite varied. For toluene, reported K_{oc} values vary from 13 to 710 [21]. Zytner [20] reported K_{oc} values in the range of 65 to 151 for toluene.

The amount of organic matter in the deep subsoils is generally low, often less than 0.1% [22], causing Banerjee et al. [23] and Schuille [24] to ascertain that the extent of contaminant adsorption in deep soils will not be controlled by the organic content of the soil. Bare clay surfaces also adsorb hydrocarbons depending upon the type of clay, the type of hydrocarbon, and the concentration of the hydrocarbon. Adsorption on montmorillonite is higher than adsorption on illite which, in turn, is higher than adsorption on kaolinite. These adsorption differences are attributed to the expandability and the large surface area of montmorillonite clay, and also to the fact that illite has a larger surface area than kaolinite. In addition, the greater the hydrophobicity and the molecular weight of the contaminant, the more likely that the contaminant will be adsorbed. Water is more strongly attracted to itself than to nonpolar organics, causing hydrophobic organics to be removed out of solution and adsorbed onto the soil surface. Hydrophobicity is measured by the octanol/water partition constant, K_{ow} , a property of the adsorbate; the higher the K_{ow} , the more hydrophobic will be the contaminant. The K_{ow} value for toluene is 490 [14].

The amount of adsorption onto soil is also dependent on the moisture content of the soil because water competes effectively for adsorption sites. The greater the saturation, the greater the displacement of the organic contaminant by water as depicted in Fig. 1. This displacement occurs because of a strong dipole interaction between the water molecules and the polar surface of the soil particles, which inhibits nonpolar VOC adsorption [25]. The strong polar interactions then predominate due to relatively weak van der Waals forces between the adsorbed VOC and the mineral surface [26]. As water

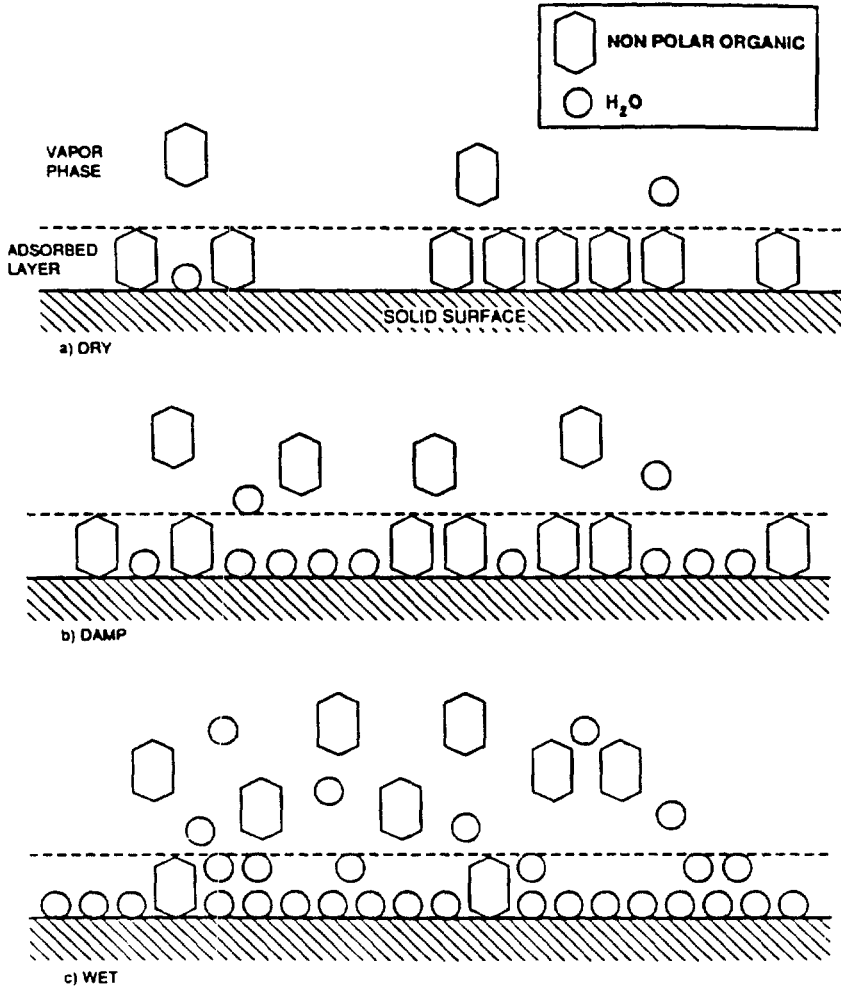


Fig. 1. Effect of moisture content on adsorption of soils [15].

passes through the system, NAPL is displaced until it reaches the point where it is bound too tightly to be easily displaced. The degree to which displacement occurs also depends on the fluid viscosity and the soil permeability.

Among the different adsorption isotherms reported in literature, the Freundlich isotherm is commonly used for describing the relationship between the adsorbed nonpolar organic contaminant on the soil and the concentration of the contaminant in solution at equilibrium [20]. This isotherm is expressed mathematically as:

$$C_s = KC_e^N \tag{4}$$

where C_s = mass of contaminant adsorbed per mass of sorbent (mg/kg), K = sorption equilibrium constant (mg/kg)(mg/l)^{-1/N}, C_e = solution concentration at equilibrium after sorption (mg/l), and N = constant describing adsorption intensity. The higher the

K and N values, the greater the sorption capacity of the medium. In order to determine K and N , the above isotherm equation is linearized by expressing it in logarithmic form as follows:

$$\log C_s = \log K + N \log C_e \quad (5)$$

where $\log K$ is the intercept and N is the slope of the straight line described by the $\log C_s$ and $\log C_e$ data. The exponent N is an indicator of whether adsorption remains constant at different equilibrium concentrations. If N equals one, a linear relationship exists between equilibrium concentration and the amount of contaminant adsorbed; if N is less than one, adsorption decreases with increased contaminant concentration levels; and if N is greater than one, adsorption increases as equilibrium concentrations increase. The hydrophobic organic contaminants exhibit a linear relationship between the contaminant adsorbed to the soil and the equilibrium concentration in the aqueous phase if their concentrations are below 10^{-5} mole/l, or less than one-half the water solubility, whichever is lower [27]. However, if the contaminant concentrations are higher, the assumption of linearity could overpredict the amount of contaminant adsorbed [25].

Kinetically, the adsorption process proceeds in two steps: fast adsorption onto external surfaces, and then slow diffusion into the interstices of soil grains [28]. Adsorption rates are slower for larger soil aggregates and for more hydrophobic compounds, with higher K_{ow} partition coefficients, due to lower intra-particle diffusivities. The adsorption process may require long time periods for equilibration, possibly several weeks or months, due to the long diffusive path lengths and/or high micro-scale retardation. Wu and Gschwend [29] reported desorption experiments using river sediments and demonstrated that the adsorption process is reversible. This study also showed that this desorption process has a similar time scale to that of adsorption for achieving equilibrium conditions.

The adsorbed contaminants must be desorbed before they dissolve and/or volatilize during air sparging. Schwarzenbach and Westall [30] stated that adsorption of nonpolar organics is reversible for the concentrations that are found in natural waters. This statement appears to be correct based upon the adsorption of nonpolar organics being greatest when the soil organic content is highest and the soil moisture content is lowest. The vadose zone is more likely to have soil with higher organic carbon content and is therefore more likely to adsorb VOCs. While the adsorption is greater in the unsaturated zone, volatilization also dominates in this zone. If large quantities of VOCs are adsorbed in the saturated zone, desorption and dissolution will be required to facilitate contaminant removal during air sparging. However, the low adsorption tendencies of hydrophobic organic contaminants in aquifers are generally favorable for effective removal by air sparging.

2.2. Contaminant transformation mechanism: biodegradation

Biodegradation is a contaminant transformation mechanism that can occur in both the saturated and unsaturated zones of the subsurface. The majority of compounds in petroleum products are biodegradable [31]. Considerable debate on the importance of biodegradation during air sparging has taken place and most air sparging models neglect the biodegradation [11,13,32] due to the significant amounts of dissolved oxygen (DO)

needed to cause complete mineralization of the organic compounds [31]. The amount of oxygen required for complete mineralization of one gram of hydrocarbon ranges from three to three and a half grams [33]. Even when pure oxygen is injected, 75 000 kilograms of water must be delivered to the subsurface in order to mineralize one kilogram of fuel hydrocarbons [31]. Other factors that affect the biodegradation include the temperature and the rate of air injection. Heated air may increase microbial growth, thereby enhancing the biodegradation of the contaminants [6]. Injected air increases the DO levels; however, higher injection pressure may limit oxygen enrichment by preventing the formation of bubbles. Limiting the vacuum pressure in extraction wells has been suggested as a method that would enhance the dissolution of oxygen.

Chiang et al. [34] have described the reduction of benzene in a shallow aquifer from 9.83 kg to 2.25 kg over a fifteen-month period with no treatment at all. Tests conducted showed biodegradation was the most important mechanism in attenuating the contaminant. A direct relationship resembling a first order decay process was found to exist between the amount of DO and the amount of benzene, toluene and xylenes (BTX) that were present in groundwater field samples. Statistical analyses showed a high negative correlation (p -value < 0.5) between the total BTX and the natural logarithm of DO. Experimental results showed that 80–100% of BTX with levels of 120–16,000 ppb were degraded with half-life ($t_{1/2}$) of 5–20 days when DO was greater than 2 ppm. The $t_{1/2}$ of BTX degradation was 20–60 days when the DO was less than 2 ppm, and little or no degradation took place when DO levels were 0.5 ppm or below. Chiang et al. [34] postulated that a minimum DO threshold level of approximately 2 ppm exists which could sustain natural degradation of BTX by soil microbes. Felten et al. [35] reported monitoring data for a contaminated site where the DO was less than 2 ppm before the air sparging began. After sparging for 16 months, the DO increased as high as 10 ppm in some locations. The hydrocarbon-degrading bacteria count also increased from 10 to 420 times at four out of the five wells where the DO contents increased, as seen in Table 1.

Wilson et al. [36] also noted a low ratio of oxygen to hydrocarbon consumed. Malone et al. [17] postulated that the parent hydrocarbon is transformed to partially oxygenated intermediates. Higgins and Gilbert [37] suggested two possible pathways for toluene degradation or breakdown. The first pathway results from a direct aromatic ring attack and leads to the sequential formation of 2,3-dihydro-toluene and 3-methylcatechol. The second pathway is the attack of the methyl group which leads to the sequential formation of benzyl alcohol, benzaldehyde, benzoic acid, and catechol prior to ring cleavage. The incorporation of oxygen into the structure decreases the oxygen demand.

Although the amount of DO needed for effective biodegradation is still being debated, air sparging increases the dissolved oxygen content in the saturated soil zones and groundwater, which, consequently, enhances the biodegradation of the organic compounds. The benefits of biodegradation during the air sparging process have not been thoroughly quantified. Some practitioners neglect the biodegradation effects; however, under certain field conditions, these effects may be significant.

2.3. Transport mechanisms

The contaminant transport mechanisms, namely, advection, mechanical dispersion, and molecular diffusion dictate the overall removal of contaminants from the subsurface

Table 1
Dependence of hydrocarbon-degrading bacteria on dissolved oxygen [35]

WELL ID	March 1991	March 1992	August 1992
<i>GT-7</i>			
Total BTEX (ppm)	10.7	0.017	2.0
Dissolved oxygen (ppm)	NA	1.4/3.6 ^a	5.5
Hydrocarbon utilizing bacteria (CFU)	2.4×10^5	NA	1.0×10^8
<i>GT-13</i>			
Total BTEX (ppm)	NA	76	1.7
Dissolved oxygen (ppm)	NA	1.4/5.0 ^a	9.0
Hydrocarbon utilizing bacteria (CFU)	NA	7×10^3	8.7×10^5
<i>GT-14</i>			
Total BTEX (ppm)	NA	120	100
Dissolved oxygen (ppm)	NA	1.5/10.2 ^a	3.5
Hydrocarbon utilizing bacteria (CFU)	NA	4.7×10^4	5.8×10^5
<i>MW-2</i>			
Total BTEX (ppm)	1.4	0.7	1.7
Dissolved oxygen (ppm)	NA	NA	1.5 ^b
Hydrocarbon utilizing bacteria (CFU)	6.3×10^5	NA	3.0×10^4
<i>MW-3</i>			
Total BTEX (ppm)	52.9	NA	21
Dissolved oxygen (ppm)	NA	0.6/5.5 ^a	3.5
Hydrocarbon utilizing bacteria (CFU)	3.3×10^5	1.3×10^6	2.2×10^7

^a x / y Represent DO measurements before and 60 minutes after sparge activation, respectively.

^b Sample collected June 1992.

NA = Not analyzed.

CFU = Colony forming units.

during the air sparging process. Advection refers to the movement of vapors or liquids in water or air in response to a pressure gradient. The advective gas and water cause the contaminants to migrate depending on the soil permeability, which is related to the grain size distribution, the type and structure of the soil, the soil porosity, and the water content of the soil. As mentioned previously, the advective transport of the contaminants enhances the mass transfer mechanisms.

The mechanical dispersion, which is simply known as dispersion, refers to the spreading or dilution of the contaminant in either the groundwater or in the soil gas through mixing. The injected air during air sparging aids the dispersion process [32]. This dispersion of the contaminants enhances the dissolution process, but also increases the adsorption of the contaminants because of the increased contact with soil surfaces. As previously mentioned, these adsorption effects are not significant because of the low tendency of nonpolar organics to adsorb when the soil organic content is low and the soil moisture content is high.

The turbulence generated by the injected air during the air sparging process promotes both advective and dispersive transport of the contaminants thereby enhancing contami-

nant mixing. This mixing aids in removal of the dissolved contaminants from the NAPL-water interface as well as aids in the dissolution process. The advective–dispersive transport may cause migration of the contaminants into clean zones. This unwanted contaminant migration is prevented by designing an air sparging system which uses the appropriate positive and negative air pressures from the injection and vacuum pumps and by maximizing negative pressure where the contaminant concentration is greatest [4,6].

The injected air during air sparging may be trapped in the soil as depicted in Fig. 2. Even a small amount of trapped air in the soil can retard the movement of the dissolved air due to partitioning of the dissolved gas phase into the trapped gas phase [38]. However, if the advective–dispersive transport of this trapped air is promoted, it will increase the overall contaminant removal due to the significant amount of contaminant that is associated with the trapped gas phase.

The contaminants which are located in unconnected soil pores, clay interstices and interlayers, may not come in direct contact with the air passageways. Consequently, these contaminants must migrate due to molecular diffusion, simply referred to as diffusion, and they are subsequently removed by the mass transfer mechanisms as well as advective–dispersive transport. The diffusion process refers to the contaminant migration from areas of high concentration to areas of low concentration. The diffusive flux is governed by Fick's Law and also depends upon tortuosity, or the length of the transport path, in the soil. Because diffusion occurs slowly, the time required for the removal of this contamination drastically increases. An effective removal of bulk contamination, followed by a slower removal of contaminants was observed at numerous field sites. The slower removal of contaminants at later stages of air sparging was attributed to the diffusion process [11,12,33].

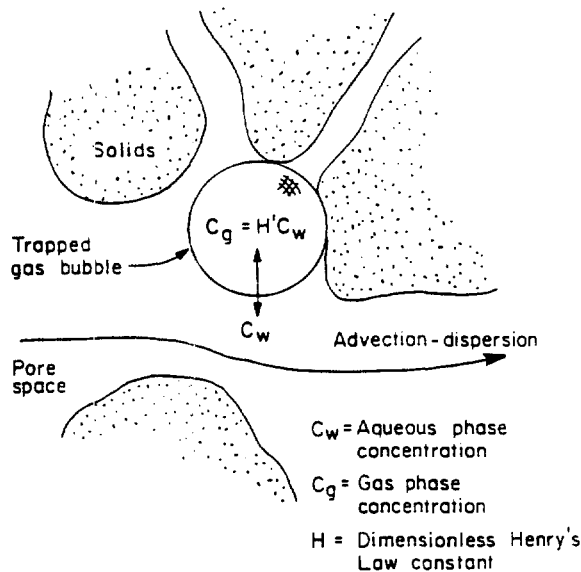


Fig. 2. Trapped gas in saturated soil [38].

Although a number of different mechanisms are responsible for the contaminant removal and transformation during air sparging, the contribution of each of these mechanisms towards the overall contaminant removal is very difficult to quantify. Controlled laboratory experiments, however, are helpful in order to investigate the relative significance of different mechanisms for contaminant removal during air sparging.

3. Laboratory experimentation

In this study, column and batch tests were performed in order to assess the mechanisms that control the contaminant removal from saturated soils during air sparging. Toluene, which is a common VOC found in petroleum products, was used as the contaminant for these tests. A brief description of the test procedures is provided below.

3.1. Air sparging experiments

An experimental program was developed with the objective of simulating the air sparging process under controlled conditions. This experimental program consisted of designing and constructing a one-dimensional column experimental set-up and then performing several tests to evaluate the effect of soil type and injected air flow rate on the contaminant removal rate. The experimental set-up and the testing procedure are described in detail by Semer [39]. A total of three tests on a fine gravel and two tests on Ottawa sand were performed with the test variables that are shown in Table 2.

A schematic of the air sparging test set-up is shown in Fig. 3. A plexiglass column, measuring 93 cm in height with an inside diameter of 8.7 cm, was used to contain the test soil. Two entry ports, one for water and the other for air, were located at the bottom cap of the column. A gas exit port was located on the column top cap. Seven septa-lined ports existed on the face of the column. The particular soil to be tested was first placed in the column from the top, and then the top cap was fitted to the column. The soil was then saturated by injecting toluene solution with a known concentration from the bottom entry port. Then, a constant water level reservoir was connected to the same port. The other entry port at the bottom cap was connected to a compressed air source, and the

Table 2
Air sparging column testing program

Test	Soil	Initial density (g/cm ³)	Initial Concentration (mg/l)	Injected air pressure (kPa)	Injected air flow rate (ml/min)
1	Fine gravel	1.62	250	6.9	380
2	Fine gravel	1.62	250	6.9	960
3	Fine gravel	1.62	250	6.9	2225
4	Ottawa sand	1.58	50	6.9	960
5	Ottawa sand	1.58	250	6.9	2225

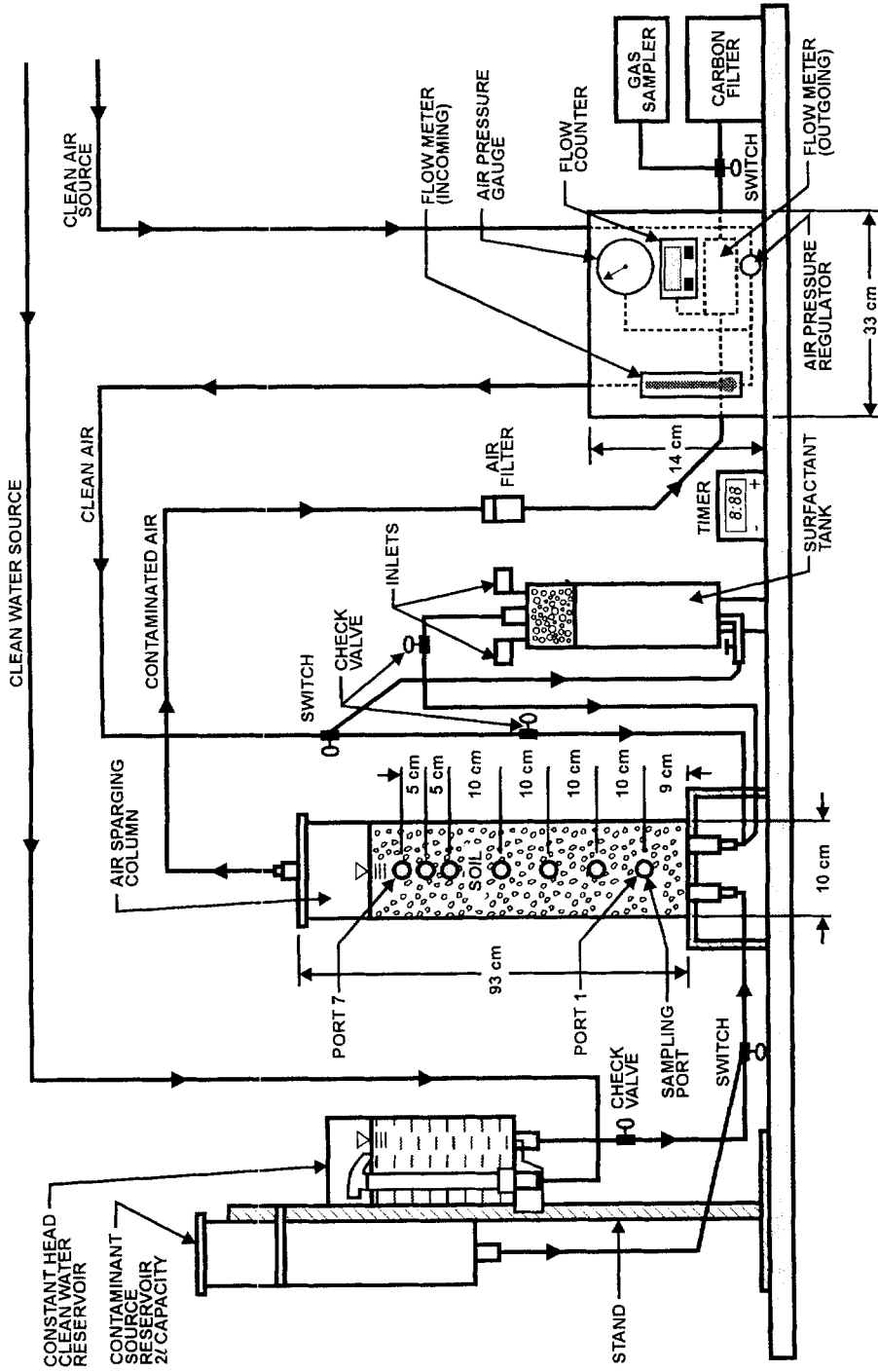


Fig. 3. Schematic of air sparging column test set-up.

compressed air was injected at a desired flow rate and pressure using regulators, gauges and flow meters.

During the testing, two microliters of contaminated water were collected from each port and injected into a gas chromatograph (GC) to determine the toluene concentration. The toluene peak was eluted in approximately 4 minutes. The procedure was repeated sequentially for each port. A time lapse of at least five minute passed between sample injections. The sampling and analysis of all of the ports took a minimum of 35 min for each round. The time of sampling and the toluene concentrations for each port were recorded. This data collection proceeded until either no significant concentration levels were detected or the test was terminated due to time considerations.

3.2. Adsorption testing

Adsorption testing was performed to determine the amount of toluene that was adsorbed in the Ottawa sand. For adsorption testing, stock solutions of toluene with different concentrations ranging from 4 mg/l to 1000 mg/l were first prepared. Five 40 ml vials with septa lids were filled with the stock solution of a specific concentration. Three of these vials initially contained two grams of Ottawa sand prior to filling with stock solution, and the other two vials did not contain any sand. These two vials were used as controls to account for toluene losses including volatilization and adsorption to the glass vials. The contents in vials were then mixed for 24 h using a shaker which was reported to be adequate for the equilibration of toluene in soils [40]. At the end of mixing, two microliters of solution were extracted from each vial using a syringe inserted through the septa. These samples were tested with the GC to determine the toluene concentrations. The results of the three sand filled samples were averaged and compared to the average of the two control vials. The mass of toluene that adsorbed onto the soil was calculated by multiplying the difference between the average toluene concentration in the solution in the control vials and the average equilibrium toluene concentration in the solution in the experimental vials by the volume of solution and then dividing by the dry mass of soil. This procedure was repeated with stock solutions of different concentrations.

4. Results and discussion

A brief description of the air sparging and adsorption test results followed by an assessment of the different mechanisms that were responsible for the toluene removal is presented in this section.

4.1. Air sparging test results

A detailed presentation of the air sparging test results and analysis is provided by Semer [39]. The typical results of the air sparging tests that were performed with gravel and sand are shown in Figs. 4 and 5, respectively. Both tests were performed using the same initial maximum toluene concentration of 250 mg/l, the same injected air flow

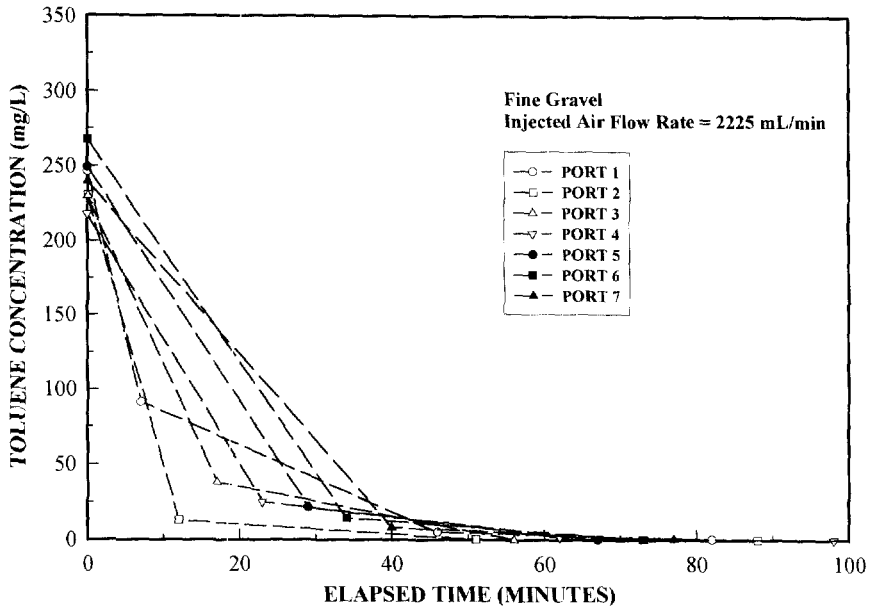


Fig. 4. Air sparging column test results for gravel with injected air flow rate = 2225 ml/min and pressure = 6.9 kPa.

rate of 2225 ml/min, and the same injected air pressure of 6.9 kPa. In both tests, complete removal of toluene was achieved; however, the time required for the complete toluene removal was 80 min for gravel and 660 min for sand. Thus, it took approximately eight times longer to completely remove the toluene from the sand. The concentration profiles are also significantly different for the sand as compared to the gravel. In gravel, the bulk of the contaminant is removed very rapidly and little tailing behavior is displayed. In sand, however, the bulk of the contaminant was removed in the first 175 min, but it took twice that amount of time to remove residual contamination.

The difference in contaminant removal rates in these two soils may be attributed to the mode of injected air migration through these soils. In gravel, the injected air was observed to travel in the form of rising bubbles. The bubbles were numerous, buoyant, and evenly distributed across the soil. The injected air flow in sand, however, was observed to travel in the form of microchannels with isolated bubbles traveling within these channels. A limited number of microchannels were observed. The majority of the contaminant in the gravel was volatilized and removed by the injected air due to the direct contact of the air with the contaminant. In sand, the contaminant that directly interfaced with the injected air was volatilized and removed; however, the contaminant that did not directly interface with the injected air had to diffuse into the microchannels prior to volatilization and final removal. This diffusion process caused a relatively slow removal rate of toluene at the lower concentrations. Thus, diffusion appeared to be primarily responsible for the increased contaminant removal time in sand.

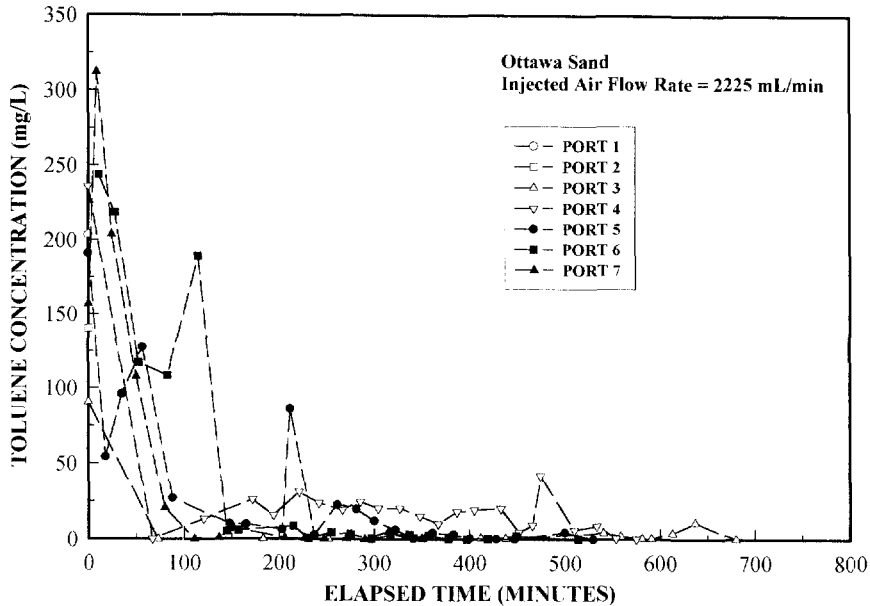


Fig. 5. Air sparging column test results for sand with injected air flow rate = 2225 ml/min and pressure = 6.9 kPa.

It is also apparent that bulk contaminant removal occurred faster in the gravel than in the sand, although the difference in removal times of the bulk contaminant in these two soils was not nearly as great as the difference in removal time which was caused by the residual contamination. This faster bulk contaminant removal may be due to higher contaminant volatilization in gravel as compared to the sand, which is a result of uniform distribution and greater contact between the contaminant and the injected air in the case of gravel.

The tests performed on gravel using different air flow rates were used to assess the effect of flow rate on the overall contaminant removal efficiency. The three tests performed on gravel, where the initial maximum concentrations of toluene were the same but the flow rate was varied, showed that an increased air flow rate decreased removal time as shown in Fig. 6. Complete contaminant removal was achieved in 390 min when the flow rate was 380 ml/min; in 140 min using a flow rate of 960 ml/min; and in 80 min when the flow rate was 2225 ml/min. The increased air flow rate also increased the amount of contaminant volatilization and the advective transport of the contaminant. When the flow rate was increased from 380 to 960 ml/min, the toluene removal occurred 2.8 times faster. However, increasing the flow rate from 960 to 2225 ml/min resulted in a removal time that was 1.8 times greater. Therefore, the toluene removal rate and the air flow rate are not directly proportional. These results show that the contaminant volatilization in gravel increases with an increase in the air flow rate, but points toward a limit to the benefits of this increased flow rate. Diffusion does not appear to play an important role in gravelly soil. The increased dissolution caused by

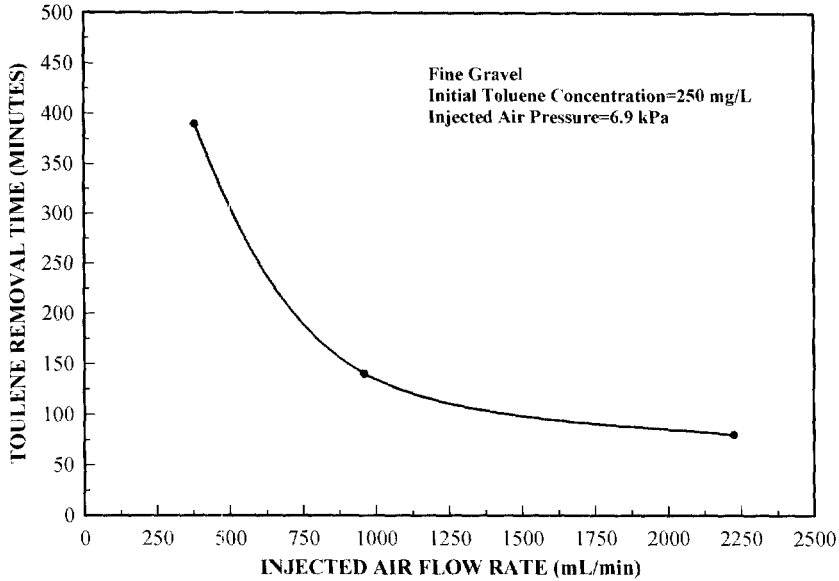


Fig. 6. Effect of injected air flow rate on contaminant removal time for gravel.

greater air turbulence at higher flow rates may also cause an increase in the contaminant removal.

When the air sparging test was repeated on the sand using a much lower initial maximum contamination level of 50 mg/l and a lower flow rate of 960 ml/min, the results showed incomplete toluene removal even after 1000 min [39]. These results demonstrate that the air flow rate has a significant influence on the removal of toluene in sandy soils. The use of a lower flow rate in sand may render the air sparging technique ineffective, possibly due to the creation of a very limited number of air passageways.

4.2. Adsorption test results

Based on the batch tests, the adsorption isotherm for toluene in Ottawa sand is plotted as shown in Fig. 7. These results show that little or no adsorption of the contaminant occurred at the lower toluene concentrations while the adsorption increased at higher toluene concentrations. The adsorption isotherm resembles as an S-type isotherm, which is indicative of organic–organic interaction at high concentrations. In this case, the toluene is more likely to bond to itself at the edges of the sand than to become attached to the sand because the sand does not contain any organic material. The air sparging experiments performed for this research used initial toluene concentrations ranging from 50 to 250 mg/l. At these concentration levels, the batch tests showed no adsorption of toluene to the sand. The fine gravel used for the air sparging experiments also did not contain any organic matter and is very likely to have a similar adsorption behavior to

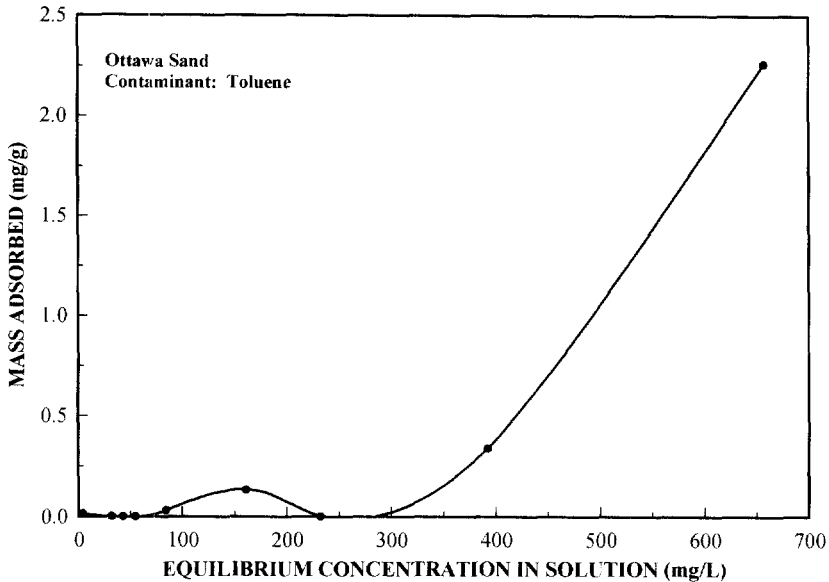


Fig. 7. Adsorption isotherm for toluene on Ottawa sand.

that of the sand. Therefore, adsorption is not considered a significant mechanism that hinders toluene removal during air sparging in these soils.

4.3. Assessment of mechanisms

As described in Section 2, the major mechanisms that can affect the removal of VOCs from saturated soils during air sparging are: (1) volatilization, (2) dissolution, (3) adsorption/desorption, (4) biodegradation, (5) advection, (6) dispersion, and (7) diffusion. Based on the adsorption test results, the adsorption of toluene in the gravel and sand tested in this study is insignificant. These soils did not contain any organic matter or clay, therefore, no adsorption of toluene was observed. Most aquifers are composed of soils with low organic matter and clay content; therefore, adsorption and desorption may not be a significant process which affects the contaminant removal during air sparging. If the contaminated field soils contain organic matter and/or clay, the effects of adsorption/desorption must be carefully evaluated. Additionally, water competes effectively with VOCs for adsorption sites. The most significant bonding of the toluene is to itself which occurs at high concentrations. Toluene clusters are then formed which are subsequently removed due to other air sparging mechanisms such as volatilization and dissolution.

Biodegradation is an important mechanism in the subsurface where natural microorganisms exist. The soils used for this study were not tested for the presence of microorganisms; however, because the soils did not contain organic matter and the experiments were short duration tests, the amount of biodegradation that would occur is

insignificant. The importance of the biodegradation that occurs during air sparging in the field soils, however, should not be underestimated. Microbes can degrade and transform contaminants in areas where air passageways have not penetrated. Biodegradation is enhanced by the additional oxygen in the subsurface even after air injection has ceased. This biodegradation is most likely to degrade the residual contamination which remains in the subsurface after the active treatment is completed. Since the dissolved oxygen may increase due to air sparging even in areas which are outside of the radius of influence of the air sparging injection well, biodegradation may also occur in areas where there is little volatilization occurring. Biodegradation is a very desirable process because it transforms the contaminants into nonhazardous constituents rather than causing a phase transfer of the contaminants.

Volatilization is the most important of all the air sparging mechanisms because it causes the contaminant to partition from the liquid phase into the vapor phase. Volatilization is governed by Henry's Law in equilibrium situations; however, during air sparging, transient air flow conditions cause a nonequilibrium situation to exist. The volatilized air is continuously removed by advective transport from the soils quite easily. The volatilization rate depends on the contaminant type, contaminant concentration, and the air flow rate. The experiments conducted for this research clearly demonstrate that the volatilization rate depends on the soil type, and volatilization is the predominant removal mechanism when contaminant levels are highest. At this time, the bulk removal of the contaminant occurs. When the contaminant concentrations are low, or when the contaminant needs to migrate from within the interstices of the soil matrix, the rate of volatilization decreases considerably. In such situations, other mechanisms, such as dissolution and/or diffusion, become important in decreasing the contamination levels.

Although dissolution occurs very slowly, is an important contaminant removal mechanism during air sparging. Generally, contaminants such as toluene do not easily dissolve even when high contaminant concentration gradients exist. The air sparging process promotes dissolution by creating turbulence which aids in mixing the contaminant and the water. The more the contaminant is dispersed into the water, the more likely the contaminant will interface with the sparged air. This increased air interface is especially important during times of high contaminant concentration when equilibrium is actually controlling the volatilization process.

Vigorous movement of the water which caused it to mix with the contaminant was more evident in the gravelly soil than in the sandy soil. For sand, the injected air in passageways could only mix the contaminant and water that was directly in its path. The toluene between passageways was left to be removed by diffusion. Diffusion is rate-controlling because diffusion driven mass flux is significantly less than the advective-dispersive mass flux. Diffusion was not a controlling mechanism in gravelly soil in the one-dimensional column experiments performed, whereas dispersion, dissolution, and volatilization were the predominant mechanisms. Dissolution was likely to have been the rate-controlling mechanism in the gravelly soil, while for sandy soil, volatilization, dispersion, dissolution, and diffusion were all controlling mechanisms with diffusion being the rate-controlling mechanism. The difference in removal time between the gravelly soil and the sandy soil was due to poor air-water contact in the Ottawa sand which was caused by channeling.

5. Conclusions

Some conclusions can be drawn based on the results of this study.

(1) The rate at which contaminants are removed during air sparging depends on the various contaminant mass transfer and transport mechanisms which include volatilization, dissolution, adsorption/desorption, biodegradation, advection, dispersion, and diffusion. These mechanisms are affected by the soil type, contaminant type and concentration, and the injected air flow rate and pressure. Quantifying the contribution of each of these mechanisms towards the total contaminant removal at any time is quite complex because of the nonequilibrium conditions caused by the injected air.

(2) For the saturated sand and gravel which were contaminated with toluene, volatilization was the most dominant contaminant mass transfer process that occurred. Therefore, for actual field conditions, the vapor pressure and Henry's constant of the contaminant will help to identify if the air sparging process would be viable. The volatilization rates depend on the distribution of the injected air in the soil.

(3) During air sparging, dissolution of NAPLs such as toluene into the dissolved phase occurs very slowly, but this dissolution is likely to increase with increased injected air movement in soils.

(4) The adsorption of the contaminant to the soils tested in this study was negligible; however, adsorption can be a significant retardation mechanism in soils which either contain large amounts of clay or have a high organic content.

(5) Biodegradation is likely to be a very important mechanism for some field sites where it may be effective for the remediation of residual contamination, but it was not significant in these experiments due to the lack of microorganisms in the test soils and the short duration of the tests.

(6) In soils where the injected air cannot be evenly distributed, contaminants will migrate into the air passageways due to diffusion. Experiments that used sand at a low injected air flow rate demonstrated the formation of only a limited number of microchannels along which the injected air flow occurred. This diffusion controlled migration of the contaminants into the air passageways occurs very slowly, causing lingering residual contamination to remain.

(7) In sandy soil, volatilization, dispersion, dissolution, and diffusion may be the major contributing mechanisms for contaminant removal with diffusion being the rate-controlling mechanism. In gravelly soil, dispersion, dissolution, and volatilization may be the most significant mechanisms with dissolution likely to be the rate-controlling mechanism.

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