

Laboratory-scale analysis of aquifer remediation by in-well vapor stripping

1. Laboratory results

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Abstract

This study is a laboratory test of the aquifer remediation concept proposed by Gvirtzman and Gorelick (1992, *Transp. Porous Media*, 8: 71–92), which involves the removal of volatile organic compounds (VOCs) dissolved in groundwater. The principle is to inject air into a well, creating air-lift pumping, which is used as a means of in-well vapor stripping. The partially treated water is separated from the VOC vapor and infiltrates back to the water table. A laboratory-scale aquifer model containing a remediation-well prototype was used to trace VOC removal over time. The removal rates of trichloroethylene (TCE), toluene and chloroform were monitored using eight triple-level observation wells. The continuous decrease of VOC concentrations in space and time was interpreted based on three processes: (1) the diffusional mass transfer between the contaminated water and the air bubbles during their rise within the well; (2) the desorption of VOCs from the solid matrix to the water phase; (3) the flow field in the saturated zone driven by the continuous water circulation between the pumping well and the recharging area. In a companion paper (Pinto et al., 1997), three-dimensional flow and transport modeling with inter-phase mass transfer is carried out to simulate these processes. © 1997 Elsevier Science B.V.

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1. Introduction

During the last decade, much effort has been devoted to studies of groundwater pollution and remediation of contaminated aquifers (Porter, 1989; National Research

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Council, 1994). In the quest for cost- and time-effective remediation methods, new remedial concepts have been introduced (Abelson, 1989; Mackay and Cherry, 1989). This laboratory investigation focuses on a remediation technique that aims to remove volatile organic compounds (VOCs) dissolved in groundwater. Common VOCs include many dense non-aqueous phase liquids, some petroleum-related aromatics, and a few hydrocarbons. Most contamination of groundwater of this type has been caused by leakage, spillage, or disposal of petroleum products, oil and industrial solvents into groundwater (Domenico and Schwartz, 1990).

The customary treatments for soil and groundwater contaminated by VOCs include: excavation of contaminated soils (Thornton and Wooton, 1982); pump and treat using air towers (McFarland, 1989; Mackay and Cherry, 1989); forced ventilation of the unsaturated zone (Baehr et al., 1989); dissolution of contaminants using cosolvents or surfactants (Vignon and Rubin, 1989; Abdul et al., 1990); biodegradation (Wilson and Wilson, 1985; Thomas and Ward, 1989; Corapcioglu et al., 1991). Each of these methods aims to treat a different part of the contaminated site (e.g. soil, unsaturated zone, or saturated zone), and each has advantages and disadvantages compared with the others. For example, the last three have the advantage of being in situ treatments, which are sometimes preferable.

As it is natural to take advantage of the volatility of VOCs by designing aeration methods, many current efforts to remediate involve injecting air into wells, namely, air sparging (Pankow et al., 1993). Focusing on air sparging for the saturated zone, three methods have lately been introduced: (1) an under-pressure vaporizer well (Herrling et al., 1990); (2) in situ air sparging involving direct injection of air into the porous media (Brown and Jasiulewicz, 1992; Angell et al., 1992; Marley et al., 1992); (3) in-well vapor stripping by injection of air and consequent air-lift pumping (Gvirtzman and Gorelick, 1992). The third technique is tested in this laboratory investigation.

The principle of the new remediation concept is to use air-lift pumping and subsurface recirculation as a means of in situ vapor stripping (Gvirtzman and Gorelick, 1992; Gvirtzman and Gonen, 1995). Air that is injected into a well creates bubbles that rise inside the well (Fig. 1). Owing to the difference between the density of groundwater outside the well and the density of the water–air–bubble mixture inside the well, a lift is created (Govier and Aziz, 1972; Taitel et al., 1980; Driscoll, 1986). During the pumping, VOCs are stripped by diffusional mass transfer from the water phase into the air bubbles. The bubbles containing VOCs are separated from the water and the VOC vapor is collected within the well, brought to the surface and treated. The partially treated water is diverted away from the well and recharged back to the aquifer by gravitational seepage through the unsaturated zone. Consequently, circulation of water is created around the well, which allows remediation of a larger aquifer volume. As water continues to circulate, the VOC concentration is further reduced. The aquifer volume that is remediated is controlled by the water pumping rate, and by designing the geometry and locations of the pumping well and the recharge gallery.

Using the Gvirtzman and Gorelick (1992) method, the remediation efficiency should mainly depend on rates of two mass transfer processes: (1) diffusional mass transfer of VOCs from water to air bubble; (2) desorption of VOCs from solid matrix to water. Following are the essential parameters involved in these two processes.

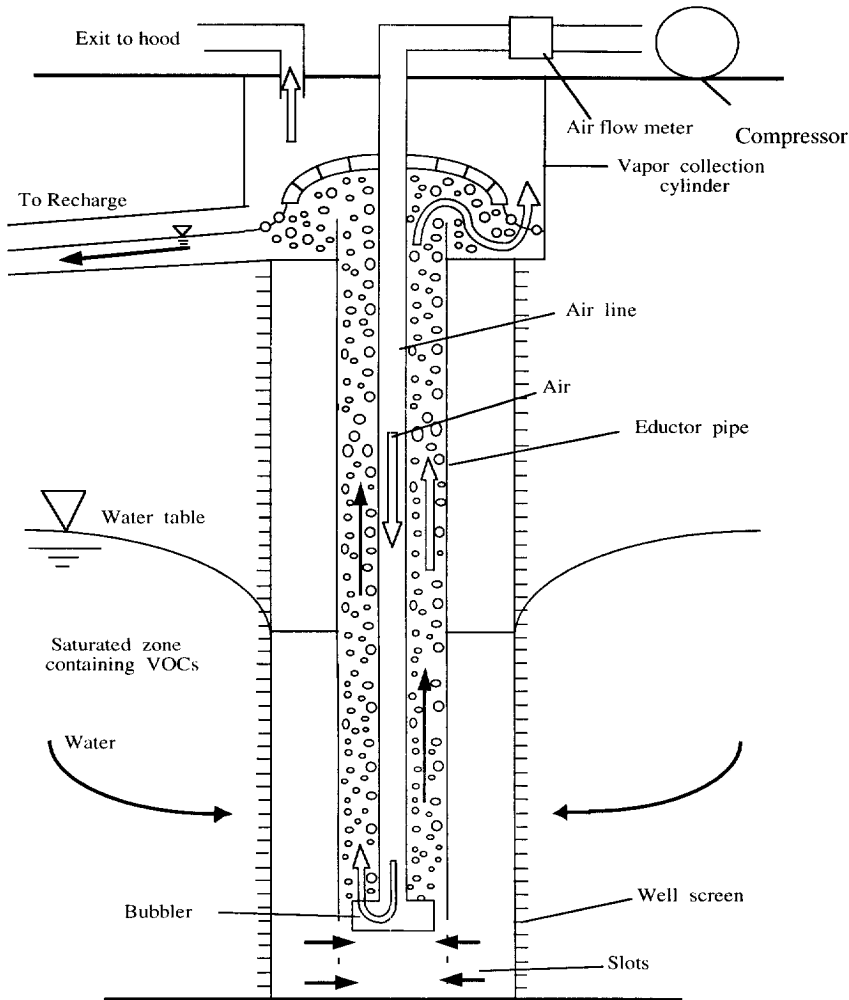


Fig. 1. Schematic configuration of a remediation system, in which air-lift pumping is used as a means of in-situ vapor stripping. Water (solid arrows) is lifted in the well, is diverted away from the well, infiltrates through the unsaturated zone back to the aquifer, and flows back to the well. Air (outlined arrows) is injected into the well, and bubbles rise and are collected at the top of the well (after Gvirtzman and Gorelick (1992)).

The efficiency of the VOC mass transfer between water and gas bubbles depends on the equilibrium partitioning coefficient described by Henry's law (Dilling, 1977):

$$H = \frac{C_{\text{air}}}{C_{\text{water}}} = \frac{16.04 P_v M}{TS} \quad (1)$$

where H is Henry's coefficient (dimensionless), C_{air} and C_{water} are VOC mass concentrations in the air and water phases (g m^{-3}), respectively, P_v is the vapor partial pressure (mm Hg), M is the molecular weight of the solute (g mol^{-1}), T is temperature

(K), and S is the equilibrium solubility of the solute in water (g m^{-3}). As equilibrium may not be achieved during the short flow duration within the well eductor pipe, concentration of VOCs in air bubbles may be less than predicted by Eq. (1).

While flowing up the well, the concentration of VOCs, C_{air} , in the bubbles increases. For volatile substances, the rate of mass transfer from the liquid to the gas phase is 'liquid-phase-controlled' (Mackay et al., 1979). Assuming a first-order mass exchange, during vertical flow along a length of pipe (dz , m), a change in vapor concentration in the bubble is described by (Gvirtzman and Gorelick, 1992)

$$\frac{dC_{\text{air}}}{dz} = \frac{K_L a_b A}{Q_{\text{air}}} \left(C_{\text{water}} - \frac{C_{\text{air}}}{H} \right) \quad (2)$$

where K_L is the diffusional liquid mass transfer coefficient (m s^{-1}), a_b is the specific bubble surface area per unit volume of mixture ($\text{m}^2 \text{m}^{-3}$), Q_{air} is the volumetric gas flow rate ($\text{m}^3 \text{s}^{-1}$), and A is the cross-sectional area of the pipe (m^2). In most laboratory experiments, all parameters that appear in Eq. (2) are measurable, except the mass transfer coefficient, K_L . Estimation of K_L is possible using the semi-empirical approach of the dimensionless Sherwood number (Skelland, 1974). Then, the mass transfer coefficient is assumed linearly proportional to the diffusivity of the dissolved VOC, D_L ($\text{m}^2 \text{s}^{-1}$).

While an aquifer is remediated, it is necessary to remove VOCs dissolved in the water phase as well as those adsorbed on the solid matrix. Consequently, a second process determining the remediation efficiency is the desorption of VOCs from the solid matrix. The partition of a VOC between water and solid phases at equilibrium is often defined by (Freeze and Cherry, 1979)

$$K_d = \frac{\bar{C}_{\text{solid}}}{C_{\text{water}}} \quad (3)$$

where C_{water} (g m^{-3}) and \bar{C}_{solid} (g kg^{-1}) are solute concentrations in water and on the solid surface, respectively, and K_d ($\text{m}^3 \text{kg}^{-1}$) is the solid–water distribution coefficient. The delay in solute transport resulting from the adsorption is defined by R (dimensionless), the retardation factor, and calculated by (Freeze and Cherry, 1979)

$$R = \frac{V_{\text{water}}}{V_{\text{contam}}} = 1 + \frac{\rho_b K_d}{\theta} \quad (4)$$

where V_{water} and V_{contam} are the average linear velocities (m s^{-1}) of water and contaminant, respectively, ρ_b is the bulk density of the aquifer material (kg m^{-3}), and θ is the porosity of the aquifer (dimensionless). When the rate of change in concentration owing to sorption is much slower than the change owing to advection–dispersion such that equilibrium cannot be reached, then a kinetic model is more appropriate. In a kinetic model, the rates of sorption and desorption are incorporated in the transport equation (Fetter, 1993).

The objectives of this research were: (1) to test this remediation method by building a laboratory-scale prototype; (2) to provide a detailed description of the remediation processes by running controlled laboratory experiments. In a companion paper (Pinto et

al., 1997), numerical simulations of three-dimensional flow and transport with inter-phase mass transfer are carried out.

2. Material and methods

The experimental system has been described in detail in an earlier paper (Gvirtzman and Gonen, 1995), to which the reader is referred. What follows is a brief description of this system.

2.1. The aquifer model

The experimental apparatus is illustrated in Fig. 2. It included a laboratory-scale aquifer model, in which a well prototype, a recharge area, and eight observation wells were constructed. The container was made of Plexiglas walls, with outer dimensions of $2.5\text{ m} \times 0.7\text{ m} \times 1.0\text{ m}$, and inner dimensions of $2.45\text{ m} \times 0.65\text{ m} \times 0.98\text{ m}$. The central part of the container, of 2 m length, containing the porous material, was separated from two water tanks at both sides of the aquifer by a dense stainless steel screen supported by beehive-like construction. Water table level in the aquifer was regulated by the water levels in both sidetanks using vertically adjusted overflow outputs. The tank was

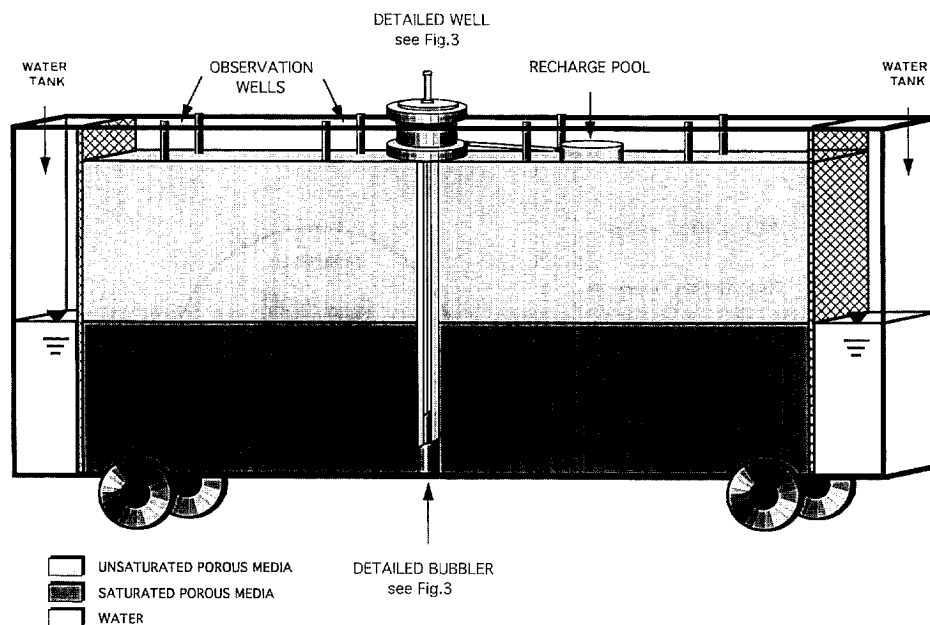


Fig. 2. The aquifer model, of 200 cm length, 65 cm width and 100 cm height, includes the remediation-well prototype and eight observation wells. The aquifer, full of sand, contains an unsaturated zone of 50 cm thickness, overlying a saturated zone of 50 cm thickness. The groundwater table is controlled by the water levels at the two storage tanks.

Table 1
Aquifer material characteristics

Parameter	Symbol	Value	Units
Particle density ^a	ρ_s	2650 ± 10	kg m^{-3}
Bulk density ^a	ρ_b	1850 ± 50	kg m^{-3}
Porosity ^a	n	0.30 ± 0.02	–
Hydraulic conductivity ^{a,b}	K	150 ± 10	m day^{-1}
Groundwater level ^b	h	0.500 ± 0.001	m
Saturated-zone pore-water volume ^c	V_w	195 ± 12	liter
Saturated-zone solid mass ^c	M_s	1200 ± 30	kg

^a Measured in columns filled with aquifer material.

^b Measured using the aquifer model itself.

^c Calculated using the container dimensions and the above measured parameters.

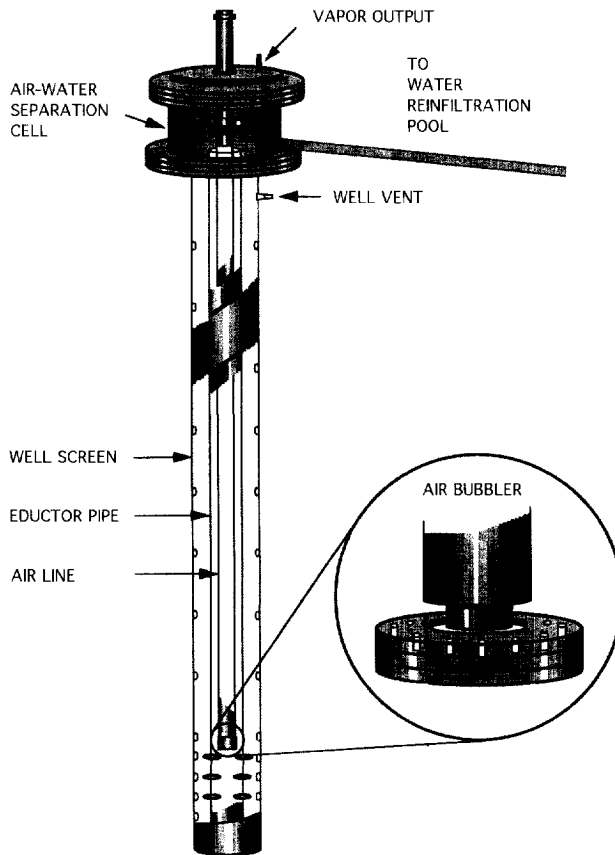


Fig. 3. Schematic diagram of the remediation well, made of three pipes: an inner air injection line, an outer well casing, and a middle eductor pipe. Bubbles are released through the air bubbler (enlarged scheme). The mixture of water–air–bubbles stops for a short duration at the separation cell, from which vapor is desorbed, and the treated water is diverted into the recharge pool.

partially filled with water, creating a saturated zone of 0.50 m thickness, overlain by an unsaturated one of 0.50 m thickness. Coarse quartz sand from Makhtesh Ramon quarry (Negev, Israel), of 0.5–0.8 mm diameter, which had been washed thoroughly, was used in the experiments. The properties of the aquifer material are summarized in Table 1.

2.2. The well prototype

An air-lift pumping well, made of Plexiglas pipes, was constructed and placed in the center of the aquifer model. It included three pipes, one inside the other (Fig. 3). The outer pipe (outer diameter (OD) 60 mm, inner diameter (ID) 50 mm) was the well casing, which was fully screened and further wrapped with fine stainless steel screen, preventing grains from entering the well. The inner pipe (OD 13 mm, ID 9.4 mm) was an air line, through which air was injected into the well. The middle pipe (OD 30 mm, ID 24 mm) was an eductor pipe, through which a mixture of water and air-bubbles was lifted. The injected air was released at a depth of 40 cm below the water table, through a bubbler (OD 20 mm), containing a dozen holes of 0.3 mm diameter (Fig. 3), creating tiny bubbles that rise. The air injection rate was controlled by a pressure valve and was measured by a flow-meter.

Water and air bubbles were lifted in an eductor pipe of 1.0 m length, which passed through 0.40 m of the saturated zone, 0.50 m in the unsaturated zone, and 0.10 m above the soil surface, entering a water–air separation cylinder. In this chamber, the water remained for a short period, and thus air bubbles were released upwards into the chamber space (Fig. 3). Then, the air containing the VOC vapor from the popped bubbles was transferred into a laboratory hood. The pumped water was diverted away from the well and was poured over the surface through a circular recharge zone (60 mm radius) and infiltrated through the unsaturated zone back to the aquifer.

2.3. Observation wells

Eight observation wells (two rows of four wells, Fig. 2 and Fig. 4), each 10 mm in diameter, were emplaced within the aquifer model. The well casings were screened by

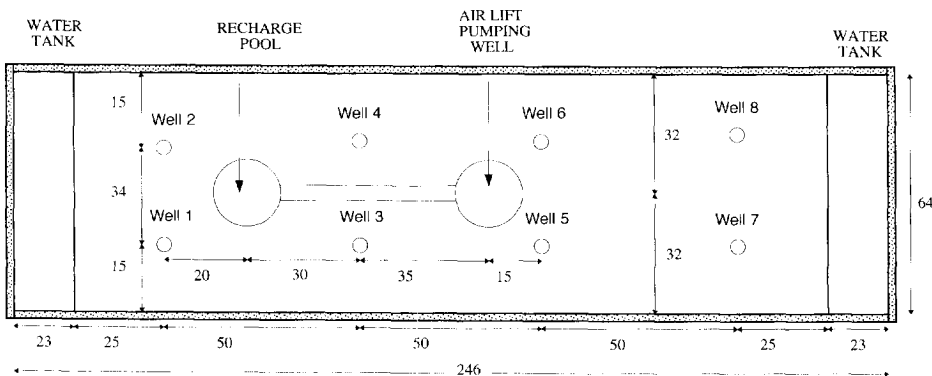


Fig. 4. Top view of the laboratory aquifer, showing the locations of pumping well, recharge pool, and eight observation wells.

holes of 5 mm diameter, along the entire saturated zone, and were wrapped with a dense stainless-steel screen, preventing grains from entering the well. Water samples were collected in these wells using a triple-level sampler, taking water from three layers of 30 mm thickness, the centers of which were located at 0.10, 0.25 and 0.40 m above the aquifer bottom. Each of the samplers included three thin elastic Tygon tubes, each reaching to one of the three depths. Each of the depth intervals was separated at its top and bottom by disks wrapped with rubber O-rings, thereby preventing vertical water mixing. Syringes and valves were connected to each of the tubes at the top of the well, from which water samples were collected.

2.4. Experimental conditions

Three compounds were used: trichloroethylene (TCE), chloroform and toluene. Their properties are summarized in Table 2. The source solution for the experiment was prepared by dissolving the VOCs in methyl alcohol and then dissolving the solution in water. In this way, an emulsion did not form. For health and safety reasons, concentrations were always lower than 5 ppm in all experiments.

One day before the start of the experiment, the source solution was introduced into the aquifer through the storage tank on one side of the aquifer. The original clean water was displaced, such that the aquifer was totally contaminated. During the introduction process, some VOC mass have lost owing to evaporation; therefore, to determine the initial conditions of the experiment, 24 samples of water for chemical analyses were collected throughout the aquifer.

The remediation experiment was started with a horizontal water table, located at 50 cm above aquifer base. The temperature was 22°C throughout the experiment. Neither influx nor outflux were introduced on any of the aquifer sides during the experiment. A pressure of 0.05 bar over atmospheric pressure was applied to induce air flow at a rate of $7.0 \pm 0.51 \text{ min}^{-1}$, which resulted in air-lift water pumping at a rate of $0.75 \pm 0.051 \text{ min}^{-1}$. The pumped water was recharged back to the aquifer at the same rate, creating internal circulation. These rates were held constant throughout the experiment, which lasted 48 h. Water samples were collected from three horizons at each of the eight observation wells, and from the two water tanks on the two sides of the aquifer. Water samples were collected using disposable plastic 10 ml syringes, and immediately afterwards were stored in 9 ml glass containers, covered with Teflon disks and screw-on caps, wrapped with Parafilm, and placed in the refrigerator at 4°C for less than 3 weeks.

Table 2
Properties of VOCs used in the experiments

Compound	Formula	MW (g mol^{-1})	Density (gml^{-1})	Solubility(mg l^{-1})	Henry's constant (at 22°C)
TCE	C_2HCl_3	131.39	1.455	1100 ^a	0.38 ^c
Chloroform	CHCl_3	119.38	1.489	784 ^a	0.14 ^c
Toluene	C_7H_8	92.14	0.901	515 ^b	0.25 ^c

^aDilling (1977).

^bBaehr et al. (1989).

^cFalta et al. (1989).

2.5. Analytical procedure

Preparation of standard solutions and calibration of analytical equipment were carried out following the guidelines of the US EPA Method 601 for purgeable halocarbons and Method 602 for purgeable aromatics (Longbottom and Lichtenberg, 1982). A known standard solution was run at the beginning and end of each day to verify the system's stability. Total analytic errors are estimated to be $\pm 8\%$; including $\pm 3\%$ for the system calibration, and $\pm 5\%$ for instrumental errors (reproducibility).

Monitoring equipment, placed in the same room as the experimental setup, included a complete gas chromatograph system. VOCs dissolved in water were stripped using a Purge and Trap Concentrator, Tekmar LSC 2000 (Cincinnati, OH, USA). Then, samples were automatically injected into a Perkin Elmer Autosystem Gas Chromatograph (Norwalk, CT, USA), separating the compounds and determining their concentrations. Helium was used as a carrier gas, using a column of 20 feet length and 1/8 in inner diameter, packed with PT 10% Alltech At-I 000 (Deerfield, IL, USA) on Chromosorb W-AW, 80/100. Compressed air and H₂ (produced by a Packard (Downers Grove, IL, USA) 9200 Hydrogen Generator) were used for burning at the flame ionization detector. The whole system was controlled by a Perkin Elmer Nelson (Norwalk, CT, USA), 1020 GC Plus Integrator.

3. Results and discussion

3.1. Variations in VOC removal rate

Changes in concentrations of TCE, chloroform and toluene at 12 points sampled during 48 h of air-lift pumping are presented in Fig. 5. These sampling points are located on a vertical plane, which represents a cross-section through the aquifer (Fig. 2 and Fig. 4). This cross-section includes four observations wells (Wells 2, 4, 6 and 8), each with three sampling horizons (top, middle, bottom). The data from the other line of wells (Wells 1, 3, 5 and 7) exhibited the same patterns and are not presented here. The reduction in VOC concentration in the course of time demonstrated the removal process from various parts of the aquifer.

As can be seen (Fig. 5), initial concentrations of VOCs in the aquifer were not absolutely uniform. Rather, slight variations were detected at the 24 sampling points. Average initial concentration and standard deviation of TCE were 2.45 ± 0.6 ppm; those of chloroform were 3.31 ± 0.6 ppm; and those of toluene were 2.0 ± 0.5 ppm. These variations resulted from the slight concentration variations in the source solution which was continuously injected into the aquifer and from evaporation losses. They also reflect the $\pm 8\%$ measurement error and differential sorption. When air-lift pumping was started, circulation within the aquifer was initiated, and thus these initial variations redistributed over time. It seems that the observed increases in VOC concentrations during the first 2 h at Well 6, for example, were the result of this effect. Such observations were detected in Wells 3 and 5 as well.

The remediation rate at a given point and at a given time can be qualitatively defined by the curve slope (Fig. 5). The general pattern, observed everywhere for the three

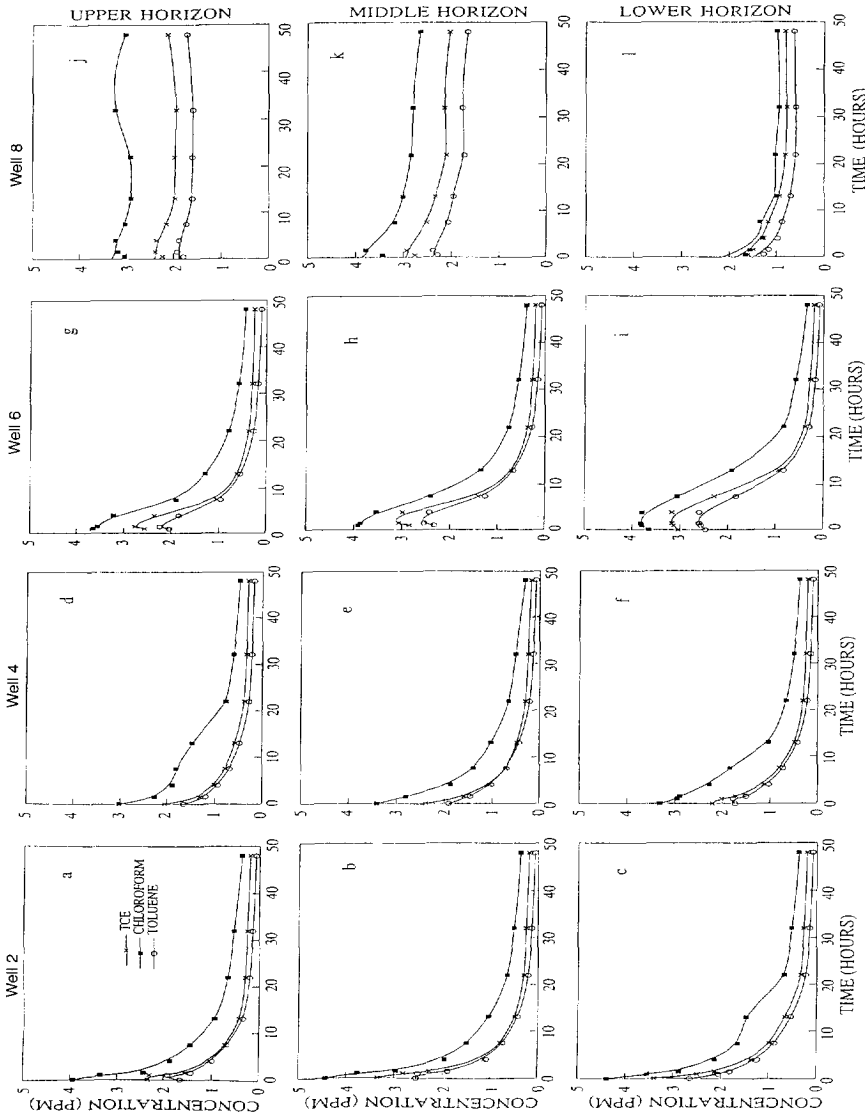


Fig. 5. Concentrations of trichloroethylene (X), chloroform (■) and toluene (O) vs. time in four observation wells, each at three horizons, demonstrating the reduction of VOC concentrations in the course of time at different parts of the aquifer owing to the application of the new remediation technique.

compounds, is a decrease in remediation rate (i.e. in curve slope) with time. This phenomenon is expected, as VOC removal rate is linearly proportional to the departure from the equilibrium concentration between the contaminated water and the clean air that is injected into the well. Therefore, as VOC concentration decreased, the mass transfer rate in the well, and thereby in the whole aquifer, decreased as well.

In addition, removal rates at a given time at various locations in the aquifer exhibited significant variations. For example, during the first 10 h of the experiment, remediation efficiencies observed in Wells 2 and 4 (Fig. 5(b), Fig. 5(e)) were higher than those observed in Well 6 (Fig. 5(h)). Also, these three wells were much more efficient in VOC removal than Well 8 (Fig. 5(k)). Moreover, even at a given well, remediation efficiencies varied between different horizons. For example, at Well 6 (Fig. 5(g–i)), during the first 10 h of the experiment, VOC concentrations were reduced at a high rate in the upper horizon, at a middle rate in the middle horizon, and at a low rate in the lower one. This phenomenon was observed also in Well 8 (Fig. 5(j–l)).

These results demonstrated the temporal and spatial variations in VOC removal rate. Understanding of these phenomena is possible by quantifying the involved processes. For this purpose, several batch experiments were carried out: sorption isotherms have been determined to quantify the mass distribution and transport retardation, degrees of vapor saturation were measured to quantify the in-well VOC stripping, and other control experiments were conducted to determine VOC mass losses. These experiments are described in the following sections. Finally, flow and transport models were used (Pinto et al., 1997) to quantify the circulation pattern in the aquifer.

3.2. VOC sorption on solid surfaces

The solid–water partition coefficients, Eq. (3), for our sand-box aquifer were determined experimentally by building the equilibrium sorption isotherms. Aliquots of the three VOCs, in various concentrations ($2\text{--}10\text{ mg l}^{-1}$), were well mixed and shaken with the sand for 48 h, and the amounts of VOC removed were determined. Results are shown in Fig. 6. It is evident that very small amounts of VOCs were adsorbed on to the aquifer; that is probably because the aquifer material consisted of well-washed coarse quartz. Calculated parameters of K_d and R are summarized in Table 3.

Mackay et al. (1985) stated that the retardation factors of most common groundwater contaminants are expected to fall in the range of 1–10 for many sand and gravel aquifers

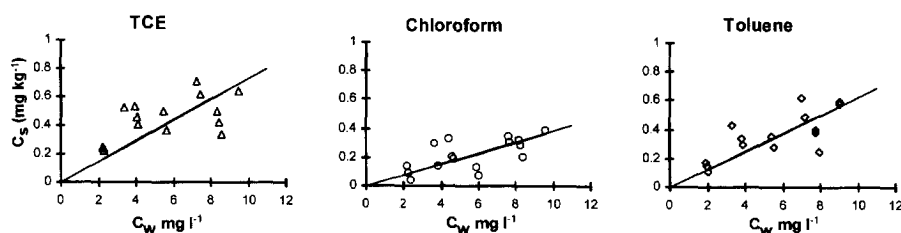


Fig. 6. Sorption isotherms of trichloroethylene, chloroform and toluene onto the sand aquifer material, and their linear regression lines.

Table 3
Parameter estimation of VOC water–solid distribution

Parameter	Symbol	Unit	TCE	Chloroform	Toluene
Partition coefficient	K_d	kg^{-1}	0.06 ± 0.02	0.03 ± 0.02	0.05 ± 0.02
Retardation factor	R	–	1.4 ± 0.1	1.2 ± 0.1	1.3 ± 0.1

that are low in their solid organic matter content. Actually, a narrower range (1.5–3.0) was reported for TCE in some field studies of sandy aquifers (Roberts et al., 1986; Mackay et al., 1994). Our calculated values are in accord with these results.

3.3. Degree of vapor saturation

The objective of the following section is to determine the degree of vapor saturation in air bubbles at the top of the well. As VOCs are transferred within the well eductor pipe only from the water phase into the gas phase, mass balance calculations are possible. Comparing the total VOC mass at the bottom and top of the well, one can formulate mass balance as

$$Q_a C_{a,b} + Q_w C_{w,b} = Q_a C_{a,t} + Q_w C_{w,t} \quad (5)$$

where Q ($\text{m}^3 \text{s}^{-1}$) is volumetric pumping rate, C (g m^{-3}) is VOC concentration, a and w denote air and water, respectively, and b and t denote bottom and top of well, respectively. As the injected air released at the well bottom is free of VOCs, then $C_{a,b} \equiv 0$. Rearrangement of Eq. (5) gives

$$C_{a,t} = \frac{Q_w (C_{w,b} - C_{w,t})}{Q_a} \quad (6)$$

The actual VOC concentration in the air phase at the top of the well, $C_{a,t}$, is not necessarily under equilibrium with the VOC concentration in the water, $C_{w,t}$. Indeed, the residence time during which the air–water mixture flowed from the bottom to the top of the well is about 2.5 s (based on Q_a , Q_w and ring cross-sectional area, A , of the eductor pipe). This is probably too short a time to allow chemical equilibration between the two phases. Let us denote the concentrations in air-bubbles and in water at top of the well under theoretical equilibrium conditions by $\tilde{C}_{a,t}$ and $\tilde{C}_{w,t}$, respectively. Given a long enough pipe, such conditions may be found. Then, Eq. (5) becomes

$$\frac{C_{w,b} - \tilde{C}_{w,t}}{\tilde{C}_{a,t} - C_{a,b}} = \frac{Q_a}{Q_w} \quad (7)$$

Given constant volumetric flow rates, Q_a and Q_w , and a clean injected air $C_{a,b} \equiv 0$, and based on Henry's distribution coefficient, $H = \tilde{C}_{\text{air}} / \tilde{C}_{\text{water}}$, then Eq. (7) gives

$$\tilde{C}_{a,t} = \frac{C_{w,b}}{\frac{1}{H} + \frac{Q_a}{Q_w}} \quad (8)$$

The apparent degree of vapor saturation at the top of the well, S_v , in our experiment can be defined, using Eq. (6) and Eq. (8), by

$$S_v = \frac{C_{a,t}}{\tilde{C}_{a,t}} \quad (9)$$

This parameter is the key factor for determining the in-well volatilizing efficiency of the remediation system.

In our laboratory experiment, we only measured VOC concentrations in the aquifer using the observation wells. Unfortunately, in the pumping well, neither the dissolved ($C_{w,t}$), nor the vapor ($C_{a,t}$) VOC concentrations were measured. Therefore, the degree of vapor saturation became a critical parameter for performing any mass balance calculations. Consequently, three controlled ‘air-lift pumping’ experiments were set up using the well prototype within a water tank. Application of an air volumetric flow rate of 101 min^{-1} induced water pumping at a rate of 1.021 min^{-1} . Concentrations of VOCs dissolved in water at the bottom of the well and at its top were measured, and the apparent degree of vapor saturation was calculated. The results of these controlled experiments are summarized in Table 4. Although the flow conditions of the controlled experiments were slightly different from those of the aquifer (Q_a of 101 min^{-1} compared with 71 min^{-1} , and Q_w of 1.081 min^{-1} compared with 0.751 min^{-1}), both used the same well prototype, at the same water levels and with almost the same volumetric flow ratio (Q_a/Q_w of 9.2 and 9.33, respectively). Given the variations around the mean of S_v (Table 4), we assumed both had almost the same degree of vapor saturation at the top of the well. An average value of 60% vapor saturation was taken to be the resultant diffusional mass exchange during flow along an eductor pipe of 1.0 m length.

The question that arises is: why have all three VOCs demonstrated the same degree of vapor saturation of 60%? In other words: is it possible that the mass transfer kinetic rates of all three VOCs are the same? Based on Eq. (2), it seems that four parameters affect the transfer kinetics: the air flow rate (Q_a), the cross-sectional area of the eductor pipe (A), the specific bubble surface area (a_b), and the diffusional mass transfer

Table 4
Controlled air-lift pumping experiments^a

Parameter	Symbol	Unit	TCE	Chloroform	Toluene
Concentration at well bottom	$C_{w,b}$	mg l^{-1}	2.59 ± 0.14	3.01 ± 0.19	2.26 ± 0.12
Concentration at well top	$C_{w,t}$	mg l^{-1}	1.44 ± 0.04	2.05 ± 0.03	1.40 ± 0.05
Vapor concentration at well top ^b	$C_{a,t}$	mg l^{-1}	0.125 ± 0.01	0.10 ± 0.01	0.09 ± 0.01
Henry's constant at 22°C ^c	H	–	0.38	0.14	0.25
Equilibrium vapor concentration ^d	$\tilde{C}_{a,t}$	mg l^{-1}	0.22 ± 0.01	0.18 ± 0.01	0.17 ± 0.01
Apparent vapor saturation degree	S_v	–	0.57 ± 0.07	0.56 ± 0.07	0.53 ± 0.07
Molar volume	\bar{V}	$\text{cm}^3 \text{ mol}^{-1}$	93.5	77	111.3
Diffusivity in water	D_w	$\text{cm}^2 \text{ s}^{-1}$	1.04×10^{-5}	1.17×10^{-5}	0.94×10^{-5}

^aAverage values based on three experiments.

^bCalculated by Eq. (6).

^cFalta et al. (1989).

^dCalculated by Eq. (8), using $Q_a/A_w = 9.2$.

coefficient (K_L). Obviously, Q_a , A and a_b were equal for all three VOCs, as mass transfer took place at the same air injection rate, inside the same eductor pipe and into the same air bubbles. The fourth parameter, the coefficient of mass transfer, is linearly dependent on the diffusivity of the compound in water (Skelland, 1974), and the latter can be calculated by (Schwarzenbach et al., 1993)

$$D_w = \frac{13.26 \times 10^{-5}}{\mu^{1.14} \times \bar{V}^{0.589}} \quad (10)$$

where D_w is the diffusivity of VOC in water ($\text{cm}^2 \text{s}^{-1}$), μ is the water viscosity (cp), and \bar{V} is the VOC molecular volume ($\text{cm}^3 \text{mol}^{-1}$). The molecular volumes of the three VOCs are presented in Table 4 (based on Schwarzenbach et al. (1993)). At a temperature of 22°C, the water viscosity is 0.89 cp, and values of D_w were calculated (Table 4). As can be seen, there is no significant difference between the three VOCs. This explains the almost equal mass transfer kinetics and degree of vapor saturation.

The stripping efficiency of 60% is obviously restricted to our tank experiment apparatus. Based on Eq. (2), it seems that better efficiencies may be achieved using: (1) a longer eductor pipe, which will extend the lifting time available for mass exchange; (2) smaller bubbles having larger specific surface area (a_b); (3) slower air flow velocity (Q_{air}/A), which also will extend the time available for mass transfer; (4) faster mass transfer coefficient (K_L), which is obviously compound dependent and temperature dependent.

3.4. VOC mass losses

Two control experiments were conducted to determine mass losses. In the first, we have measured VOC concentrations at the bottom and top of well, and at the recharge pool, while water was pumped by air-lifting. This experiment was run under a wide range of air injection rate. Results indicated that concentrations were reduced from bottom to top of well by 32–44%. More (by 5–10%) reduction of the remaining VOC concentrations took place at the recharge pool.

In the second control experiment, similar initial conditions to those of the main experiment (Fig. 5) were determined, but no air-lift pumping was applied. It was found that the initial concentrations remained the same throughout the 48 h of monitoring. This experiment verified the assumption that no VOCs were removed by bioremediation or by direct evaporation from the water table surface. Therefore, it may be concluded that the inwell air sparging, induced by the air-lift pumping, was the main reason for the reduction in VOC concentration shown in Fig. 5.

3.5. Removal rate of different VOCs

Comparing the concentration reduction rates of the three compounds at the same time and point shows that each of the VOCs behaved differently. For example, at the first stage of the experiment (the first 10 h), TCE concentrations decreased faster than those of chloroform. However, later (at 20–48 h), TCE concentrations decreased slower than

those of chloroform (Fig. 5d–i). The objective of this section is to qualitatively explain these observations.

One should note that the effective removal of VOCs depends on two processes: (1) volatilization into the air bubbles inside the well; (2) desorption from the aquifer matrix into groundwater. Actually, desorption, which slows down remediation, and volatilization, which accelerates it, are two competing processes which compensate each other during remediation. Comparing TCE and chloroform, they have opposite properties: TCE tends to volatilize, and also tends to adsorb; whereas, relatively, chloroform tends neither to volatilize nor to adsorb. Therefore, TCE is quickly removed within the well, but is adsorbed on the solid matrix, retarded in the aquifer, and thus its effective removal slows down. Chloroform, on the other hand, behaves differently: it does not volatilize quickly, but as it is not so strongly adsorbed and retarded in the aquifer, its effective removal almost equals that of TCE.

It is hypothesized that one of these two processes becomes the limiting step at specific times and places, and the other becomes the limiting step at other times and places. For example, in the aquifer space adjacent to the well, the retardation effect is negligible, and thus the volatilization capability becomes the limiting step; whereas away from the well, the retardation effect becomes the limiting step. Likewise, each of the two processes becomes the limiting steps at different times. At the first stage of the experiment, when water entering the well came from the near surroundings of the well, the retardation effect may have been negligible. Therefore, the effective remediation depended mainly on the volatilization, and thus TCE removal was faster. However, during the course of time, water entering the well came from further away, so that retardation became the limiting factor. Therefore, the removal efficiency of chloroform became larger. Quantitative analysis of these processes and the resultant remediation efficiency is presented in the companion paper (Pinto et al., 1997), using a three-dimensional numerical code of flow and transport.

4. Summary

The remediation technique of using recirculating air-lift pumping as a means of in-well vapor stripping was studied. It was tested in the laboratory using a laboratory-scale aquifer in which a well prototype was constructed. Concentrations of TCE, toluene and chloroform in groundwater samples collected throughout the aquifer at various times were monitored. By the end of the 48 h experiment, initial concentrations were reduced by over 90% in most cases. It was found that the effective removal of VOCs depends on two attributes: (1) their capability to volatilize into the air bubbles inside the well; (2) their capability to desorb from the aquifer matrix into groundwater. This quantitative monitoring exhibited that the VOCs were effectively removed from the contaminated groundwater. Obviously, in field cases, where sorption and desorption play a major role, the efficiency of the method could seriously be reduced. Finally, further research is needed to test whether this technology is more efficient and cost-effective than conventional technologies such as pump-and-treat.

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