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Q. Zhang
Kansas State University

L. C. Davis
Kansas State University

L. E. Erickson
Kansas State University

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EFFECT OF VEGETATION ON TRANSPORT OF GROUNDWATER AND NONAQUEOUS-PHASE LIQUID CONTAMINANTS

Q. Zhang[1], L.C. Davis[2], L.E. Erickson[1]

[1]Dept. of Chem. Eng., Kansas State University, Manhattan, KS 66506, Phone: (785)532-5584, FAX: (785)532-7372; [2]Dept. of Biochemistry, Kansas State University, Manhattan, KS 66506, Phone: (785)532-6124, FAX: (785)532-7278

ABSTRACT

An aquifer model system was established to examine and delineate the presence, fate and transport of nonaqueous-phase liquid (NAPL) contaminants. The system consists of six independent channels with identical dimensions. The channels were constructed with steel bottoms, side panels, and end panels. Trichloroethylene (TCE) was selected as a representative compound to model NAPL groundwater contaminants in the saturated zone of the aquifer.

The flow regime of groundwater in the saturated zone was investigated by conducting a bromide tracer experiment. The movement of TCE in both horizontal and vertical directions was studied by monitoring the groundwater effluent stream and the gas phase at the soil surface after a pulse injection of liquid TCE into each channel at the bottom inlet. A multistage compartment model was developed to help interpret the experimental data and observations.

Key words: *NAPL, groundwater, transport, vegetation, trichloroethylene*

INTRODUCTION

Industrial processes related to petroleum refining, chemical manufacturing, coal coking, coal gasification, and wood processing result in the production of motor fuels, chlorinated and fluorinated hydrocarbons, coal tar, creosote, heavy oils, wood products, and waste by-products. These organic liquids are often toxic or carcinogenic and can sparingly dissolve in water, and in the context of soil and sediment contamination are termed non-aqueous phase liquids or NAPLs. NAPLs are widely distributed because of spills or leakages from storage tanks and pipe lines. The aqueous solubility of these organic liquid contaminants is low enough for them to exist in the subsurface as NAPLs but large enough to seriously degrade water quality. NAPLs in the subsurface are long-term sources of groundwater contamination and may persist for centuries before dissolving completely in adjacent groundwater. Large pools of NAPLs result from natural processes; they are of great value to the petroleum industry.

When NAPLs are released to the subsurface environment (e.g., from oil spills or leaking storage tanks), they will migrate downward from the site. After moving downward through vadose zone, some light NAPLs (LNAPLs) float and move on top of the water table, while more dense NAPLs (DNAPLs) move downward through the water table and penetrate into the saturated zone. DNAPLs such as trichloroethylene (TCE) can sink to the bottom of an aquifer and be a source of contamination for many years. In the saturated zone, NAPLs exist as pools or individual blobs that slowly dissolve into groundwater and provide a persistent source of pollutant (Mackay et al., 1989). The total mass of contaminants in saturated soil and groundwater is the sum of that in free (NAPL) phase, adsorbed phase, vapor phase, and aqueous phase.

After the initial migration following a spill, mobility of a contaminant in the aquifer is determined largely by the relative concentration of it in the water and air phases of the soil. Transport of the contaminants takes place in both water and air by convection and diffusion following dissolution from the NAPL phase.

Convective transport of contaminant in the water phase is a function of the concentration of the contaminant in the water phase and the movement of the water in the soil due to pressure gradients (Mercer and Cohen, 1990). Vertical movement in the upward direction can take place as a result of evapotranspiration or capillary rise following evaporation of water at the soil surface. Convective contaminant transport in the soil gas phase takes place when the soil gas moves as a result of several processes, e.g. rising or falling groundwater table, changes in gas phase density due to heating or cooling, air sparging, or gas production.

For NAPLs in the saturated zone of the aquifer, dissolution of the constituent from the NAPL phase to the groundwater phase has been considered to be the rate-limiting step of the entire transport process (Hunt et al., 1988; Abriola, 1989; Powers et al., 1991). For most VOCs in the unsaturated zone of the soil, diffusion through the gas phase is considered by far the predominant route of transport (Marrin and Kerfoot, 1988), and thus of loss of volatile compounds from the soil system. The rate-limiting NAPL-groundwater mass transfer has been found to be influenced by a variety of factors including NAPL properties, aquifer characteristics, and fluid movement(Powers et al., 1991; Brusseau, 1992).

While searching for cost-effective bioremediation techniques, researchers have found that plants can play an important role. Vegetation may be used to actively promote microbial restoration of chemically contaminated soils and groundwater (EPA, 1992; Aprill and Sims, 1990; Davis et al., 1993b; Narayanan et al., 1996; Zhang et al., 1996; and Walton and Anderson, 1990). With growing plants, the rhizosphere is a zone of intense microbial activity in which plant enzymes may also be active. The metabolic diversity of microorganisms and plants suggests that many xenobiotic organics can be degraded by at least some species.

Evidence is accumulating that plants have a role in the degradation of TCE and other persistent organic contaminants (Walton and Anderson, 1990; Ferro et al., 1994; Narayanan et al., 1995a; Davis et al., 1993a; Davis et al., 1993b; Newman et al., 1997; Schnoor et al., 1995; Erickson et al., 1994; Tracy et al., 1992; Shimp et al., 1993; and Schnoor et al., 1995). Plants can transpire water from the saturated soil to the vadose zone. Within the vadose zone, there may be either degradation or volatilization of the contaminant (Narayanan et al., 1995a; Narayanan et al., 1995b; and Narayanan et al., 1996). Plants transpire measurable amounts of TCE and other compounds under laboratory conditions (Davis et al., 1993a; Schnoor et al., 1995; Burken, 1996; and Davis et al., 1998), but under field conditions the actual amount of compound transpired is less. In the field, plants and associate microorganisms are more capable of degrading the compound of concern and releasing less of it to the atmo-

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sphere. Uptake and transformation of TCE in poplar tissues has been reported (Newman et al., 1997). Vegetation can, to a certain extent, enhance TCE transport, transformation, and immobilization. Our study (Zhang et al., 1996) has indicated that alfalfa plants (*Medicago sativa*) can grow well in the presence of aqueous-phase TCE up to 1-2 mM and transiently tolerate higher levels. However, Ryu et al. (1996) placed alfalfa plants in treatment bottles containing water of TCE levels from 0.09 to 0.45 mM and observed rapid photobleaching of leaves at all levels at or above 0.18 mM. These studies show that TCE in the saturated zone is not as toxic as TCE in a closed container in which the gas phase is in contact with the stems and leaves.

Our research group has been studying the fate and transport of various organic compounds in soils with plants for several years (Narayanan et al., 1995a; Davis et al., 1993a; Narayanan et al., 1995b; Davis et al., 1993b; Zhang et al., 1996; Narayanan et al., 1996; Zhang et al., 1997a; Makepeace et al., 1996; Ryu et al., 1996; and Zhang et al., 1997b). Contaminant transformations and enhanced adsorption/immobilization have been observed in soil chambers with growing alfalfa plants (Narayanan et al., 1995a and Davis et al., 1993a). Alfalfa plants survived well in contaminated soil channels and significantly increased the volatilization rate of both water and contaminants (Zhang et al., 1996 and Zhang et al., 1997a). In field studies, alfalfa roots have been found at depths greater than 10 meters (Shimp et al., 1993).

Air sparging is a relatively new technology that is being implemented at numerous sites around the country (Mercer and Cohen, 1990; Johnson et al., 1993; Lord et al., 1995; and Reddy et al., 1995). It is primarily applied to removal of VOCs or biodegradable organic compounds from groundwater aquifers. This remediation technique involves forced introduction of air under sufficient pressure to form bubbles in the groundwater. The bubbles move through the aquifer to (1) strip volatile organic hydrocarbons from the dissolved phase and from any NAPLs present along the path of the bubbles; (2) add oxygen to the water to spur *in situ* bioremediation; and (3) for certain designs, establish large circulation cells in the subsurface. After the bubbles make their way to the unsaturated (vadose) zone, a soil vapor extraction system may be used to capture the vapors for treatment prior to release to the atmosphere (Johnson et al., 1993).

We have previously reported the use of *in situ* air sparging in conjunction with vegetation (Zhang et al., 1997a and Zhang et al., 1997b). These studies focused on the effects of vegetation and air sparging on TCE flux rates entering the atmosphere. Under the conditions of our experiments, both vegetation and air sparging significantly increased TCE losses into the atmosphere.

The objectives of this study are to characterize the effects of vegetation on groundwater flow (tracer test); to examine the presence, fate, and transport of NAPL contaminant deposited in saturated zone of an aquifer during vegetation and air sparging; and to delineate the factors that affect NAPL dissolution and transport within the aquifer.

EXPERIMENTAL SETUP AND METHODS

Setup Description

To examine and delineate the presence, fate, and transport of NAPL contaminants, an aquifer model system was established. As schematically shown in Figure 1, the system consists of six independent and identical channels constructed with steel bottoms, side panels, and end panels. Each channel is 110 cm long, 10 cm wide, and 65 cm deep with soil depth of 60 cm. The channels were packed with alluvial silty sand soil (with <10% silt) collected near a landfill in Riley County, Kansas. Five channels (Ch 1,2,3,5, and 6) are planted with alfalfa and one (Ch 4) is unplanted, to allow an investigation of the impact of vegetation.

The whole system was continually illuminated with 12, cool-white fluorescent lights (40W) at a height of 50 cm above the soil. Alfalfa plants, spaced at 10 cm intervals along the channels, were harvested monthly before blooming. Distilled water was fed from water jugs to maintain a stable water supply to the system. Water flow rate was controlled under gravitational flow by adding 1L/day to each inlet water jug. The water table was kept at approximately 35 cm (measured from the bottom) by holding the outflow tubing at a constant height.

For air sparging, five air pipes had been installed at the bottoms of channels 1 and 6 prior to planting alfalfa. At the end of each pipe, an alumina gas dispersion stone was connected to distribute air into very fine bubbles. Air input volumetric rate to each channel was 2.14 $L/m^2 \cdot day$ (Zhang et al., 1997b).

The purpose of this experimental work was to obtain quantitative information on the effects of vegetation and air sparging on the movement of groundwater and contaminant under known inlet flow conditions. Emphasis was placed on the evaluation of the influence that vegetation and air sparging have on the transport and removal of contaminant. We chose TCE as a representative compound to model in this study. At field sites, TCE, perchloroethylene (PCE) and other chlorinated solvents frequently make up at least 1 to 2% of the NAPL (Boersma et al., 1995), while TCE is the most frequently found contaminant at hazardous waste sites on the EPA's National Priority List (Olsen and Kavanaugh, 1993).

Experiments and Mathematical Methods

Bromide Tracer Test

A KBr tracer solution was added to each channel at the concentration of 40.0 mg/L of Br. By switching the inlets from water jugs to KBr solution tanks, about 1.1 liters of tracer solution were added within 12 hours in the same way the water was supplied. Water samples were taken at the exits immediately after the switch and every half-day thereafter. The concentration of bromide was determined by the phenol red method with flow injection analysis techniques. This method can quickly detect bromide concentration down to 0.1 mg/L (Freeman et al., 1993).

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The time period to feed bromide tracer is not short enough for us to assume a pulse experiment, rather we can treat the input as a square wave function. According to the linear property of residence time distribution density function f(t) (Shinnar, 1987), we know that

$$C(t) = f(t) * C_f(t) \tag{1}$$

where C(t) is the outlet concentration; $C_f(t)$ is the inlet concentration; and * denotes the convolution integral.

We then utilize the Laplace transforms of C(t) and $C_f(t)$ to obtain the Laplace transform of f(t). That is,

$$f(s) = \frac{C(s)_{output}}{C(s)_{input}} \tag{2}$$

in which $C(s)_{output}$ is the Laplace transform of the groundwater outlet concentration; $C(s)_{input}$ is the Laplace transform of the tracer input function; and f(s) is the Laplace transform of density function f(t).

The Laplace transform g(s) of a function g(t) is given by

$$g(s) = \int_0^s e^{-st} g(t) dt \tag{3}$$

in our case,

$$C(s)_{input} = \int_0^s e^{-st} C_f(t) dt \tag{4}$$

$$C(s)_{output} = \int_0^s e^{-st} C(t) dt \tag{5}$$

where C(t) is the groundwater effluent concentration which was monitored over time and $C_f(t)$ is a square wave function as shown in Figure 2.

Because the data for C(t) as a function of time are discrete, we can only use numerical integration to find out $C(s)_{output}$. On the other hand, the continuous square wave function form of $C_f(t)$ allows us to obtain $C(s)_{input}$ by analytical integration over the time range of 0 to 12 hours. Consequently f(s) is obtained. From f(s), the rth moment of f(t) will be calculated (Shinnar, 1987) through the rth derivative of f(s) with respect to s, namely,

$$\mu_r = E_f(t^r) = \lim_{s \to 0} (-1)^r \frac{d^r f(s)}{ds^r} \tag{6}$$

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Because the mean residence time is the first moment of f(t), bromide mean residence time can be obtained as:

$$C_L = \frac{C_G}{H} + \frac{C_G(V_B - V_s)}{}$$ (7)

TCE Test

Initially 20 mL (29.2 g) of TCE as pure liquid was injected into each of the inlet streams at the bottoms of channels 1,2,4,5 and 6 through a syringe pump, while channel 3 was used as control to examine the effect of TCE on plants. After the injection, groundwater samples were regularly taken from the exit sampling ports with a syringe and transferred to small vials to measure the concentration of TCE. The gas-phase TCE concentration in the vial head space, (mM), was determined using a gas chromatograph equipped with a flame-ionization detector and then, according to the mass balance of TCE in the sample, we converted C_G to the liquid sample TCE concentration, C_L (mM), as follows:

$$C_L = \frac{C_G}{H} + \frac{C_G(V_B - V_S + V_J)}{V_S}$$ (8)

where H(=0.383) is the Henry's law constant of TCE; and V_B, V_S and V_J are volumes (ml) of the vial bottle, liquid sample, and the chromatograph syringe, respectively.

To monitor transfer of TCE through the vadose zone, the following strategy was adopted to obtain the gas-phase flux rates of TCE. Six identical one-end-opened containers, 400 mL in volume and 38.4 cm^2 in cross sectional area, were placed along the top of each channel at six different positions. Gas samples were taken using 1 mL gas syringes through septa in the tops of the containers 40 minutes after placement. Sample compositions were then analyzed using the gas chromatograph equipped with a flame-ionization detector.

Because TCE injection was performed within a very short time period (20 minutes) compared to the longevity of the entire test period (more than 160 days for TCE test), we can assume pulse injection of the 20 mL of TCE. Therefore, the time records of TCE effluent concentrations can be thought of as residence time distribution curves of TCE moving in the aqueous (groundwater) phase within each channel. The corresponding mean residence time of TCE moving horizontally through the saturated zone can accordingly be obtained by integrating the effluent concentration over the testing time as follows:

$$t_{TCE,L} = \frac{\int_0^\infty t C_{TCE} dt}{\int_0^\infty C_{TCE} dt} = \frac{\sum t_i C_{TCE,i} \Delta t_i}{\sum C_{TCE,i} \Delta t_i}$$ (9)

where $t_{TCE,L}$ is the mean residence time for TCE based on analysis in groundwater; and C_{TCE} is TCE concentration measured at the groundwater exit of the channel.

For TCE moving upward to the soil surface, the concentration measured in the gas collecting containers ($C_{TCE,m}$) was used to calculate the mean residence time, $t_{TCE,G}$, of TCE which exits to the atmosphere through the soil surface. Because the concentration appears in both the numerator and the denominator terms with same order in the equation of mean residence time, we can directly use $C_{TCE,m}$ to estimate the mean residence time even though the measured concentration differs from the effluent concentration at the soil surface.

Groundwater Flow Model

To help interpret the experimental data and observations, the soil channel is assumed to consist of n identical soil compartments in series, as schematically shown in Figure 3. Groundwater flows sequentially through the saturated void volume of each compartment. At the same time, upward water movement due to evapotranspiration is assumed to be uniform over the n compartments. The volumetric flow rates of water in the horizontal and vertical directions are designated as $Q_{H,i}$ and $Q_{V,i}$ ($i = 1,2,...,n$), respectively. The mean residence time for a water molecule to flow through the whole channel is t_H for horizontal flow and t_V for vertical movement.

The void volume of every compartment is V_i and

$$V_i = V_{sat,i} + V_{unsat,i} \tag{10}$$

where $V_{sat,i} = V_{sat}/n$; $V_{unsat,i} = V_{unsat}/n$. V_{sat} is the volume occupied by water in the saturated zone, which is equal to the saturated zone volume multiplied by the water volume content, q_v; V_{unsat} is the void volume of the unsaturated zone and is equal to the unsaturated zone volume multiplied by the porosity. Assuming the soil channels have porosity $\eta = 0.30$, we choose q_v as 0.30. Then,

$$V_{unsat.} = LWH_{unsat}\eta = 8.28L \tag{11}$$

$$V_{sat.} = LWH_{sat}\theta_v = 11.6L \tag{12}$$

in which L is the length; W is the width; and H_{sat} and H_{unsat} are heights of the saturated and unsaturated zones of the channel.

According to the sequential uniform flow model assumptions, we can write

$$\tau_H = \sum_{i-1}^{n} \tau_{H,i} \tag{13}$$

with the mean residence time in the ith compartment equal to:

$$\tau_{H,i} = \frac{V_{sat.,i}}{\left(Q_{H,i} + Q_{H,i-1}\right)/2} \tag{14}$$

where

$$Q_{H,i} = Q_{H,i-1} - Q_{V,i} = Q_{H,i-1} - \frac{Q_{E.T.}}{n} \tag{15}$$

in which $Q_{H,0} = Q_{in}$; $Q_{H,n} = Q_{out}$; and $Q_{E.T.}$ is the evapotranspiration rate of the channel, which was calculated from the difference of the measured channel inlet and outlet water volumetric flow rates.

Since

$$Q_{H,i} = Q_{H,i-1} - \frac{Q_{E.T.}}{n} = Q_{in} - \frac{iQ_{E.T.}}{n} \tag{16}$$

and

$$Q_{H,i} + Q_{H,i-1} = \left(Q_{in} - \frac{Q_{E.T.}}{n}\right) + \left(Q_{in} - \frac{(i-1)Q_{E.T.}}{n}\right) = 2Q_{in} - \frac{(2i-1)Q_{E.T.}}{n} \tag{17}$$

equations (13) and (14) may be written as:

$$\tau_H = \sum_{i-1}^{n} \tau_{H,i} = \sum_{i-1}^{n} \frac{V_{sat.}/n}{Q_{in^-} \dfrac{(2i-1)Q_{E.T.}}{2n}} \tag{18}$$

Therefore, given n compartments and the corresponding channel saturated zone volume occupied by water, groundwater inlet volumetric flow rate, and evapotranspiration rate, we can estimate the residence time of water flowing out as groundwater, i.e., t_H.

For the vertical water movement, the expression of $t_{V,i}$ for each compartment can be written as:

$$\tau_{V,1} = \frac{V_{sat.,1} + V_{unsat.,1}\theta_w}{Q_{V,1}}$$

$$\tau_{V,2} = \frac{V_{sat.,2} + V_{unsat.,2}\theta_w}{Q_{V,2}} + \frac{V_{sat.,1}}{\left(Q_{H,1} + Q_{H,0}\right)/2} = \frac{V_{sat.,2} + V_{unsat.,2}\theta_w}{Q_{V,2}} + \tau_{H,1} \tag{19}$$

....

$$\tau_{V,i} = \frac{V_{sat.,i} + V_{unsat.,i}\theta_w}{Q_{V,i}} + \sum_{j=1}^{i-1} \tau_{H,j}$$

in which q_w is the fraction of unsaturated zone void volume occupied by moisture; it is chosen as 0.80 in this study.

By substituting $V_{sat.,i} = V_{sat.}/n$, $V_{unsat.,i} = V_{unsat.}/n$; and $Q_{V,1} = Q_{V,2} = ... = Q_{V,i} = ... = Q_{E.T.}/n$, the above equations can be expressed in one equation as follows:

$$\tau_{V,i} = \frac{V_{sat.} + V_{unsat.}\theta_w}{Q_{E.T.}} + \sum_{j=1}^{i-1} \tau_{H,j} \qquad (i = 1,2,.....n) \qquad (20)$$

The mean residence time of the upward moving water is different for each compartment. It depends on the path from the groundwater inlet point to the soil surface for each compartment. The arithmetic average of mean residence time values of n compartments is used as the estimated upward mean residence time for the whole channel, i.e.,

$$\tau_V = \frac{1}{n} \sum_{i=1}^{n} \tau_{V,i} \qquad (21)$$

RESULTS AND DISCUSSION

Figure 4 gives the time records in terms of bromide concentrations at the channel exits responding to the input at the inlet streams. The time scale is zero when bromide feeding was started. These results suggest that similar flow patterns exist in the saturated zone for both planted and unplanted channels. However, the fraction of water flowing upward into the unsaturated zone is smaller in the unplanted channel.

Figures 5, 6, and 7 present TCE concentration profiles in the effluent groundwater streams as response to TCE injection at the channel inlets. Figure 8 gives gas-phase concentrations of TCE in containers placed over the channel soil surfaces. Notice that vegetation affects vertical TCE movement more than TCE horizontal transport. This is attributed to root water uptake and plant transpiration which enhances the upward transport of TCE. In the unsaturated zone, some TCE moves upward due to gas-phase diffusion. Thus, it may move faster than water where gas-void volume is sufficiently large to allow TCE transport by gas-phase diffusion. Air sparging increases both the groundwater and the gas-phase TCE concentrations because it enhances mass transfer and NAPL dissolution.

The mean residence times of bromide for the saturated zone and TCE for the groundwater effluent and gas-phase release are shown in Table 1. TCE took much longer than bromide to flow out of the channels in the groundwater stream. This is because TCE was present as NAPL and because of mass transfer limitation of TCE dissolution into groundwater.

When computing values of t_H by assigning various values to n (e.g., 1,2,...,18), we found that t_H varied with n, but approached to a stable value when $n \geq 6$. We chose n=2 and n=6 to estimate the

values of t_H and t_V. Values of the estimated mean residence time, t_H and t_V, are presented in Table 2 for the cases of n = 2 and n = 6. Table 3 lists the channel physical properties and values of parameters used in the n-compartment model to estimate t_H and t_V. Values of the evapotranspiration rates $Q_{E.T.}$ are averages of daily measurement data over a one-year period.

Note that the values are impacted by vegetation and air sparging through parameter $Q_{E.T.}$. Vegetation increases the upward water flow rate through transpiration. Because air sparging negatively affected the plant growth in the initial period when TCE concentration in the saturated zone was higher, the vegetated and air-sparged channel has lower averaged upward water flow rate compared to the channel with vegetation only (Zhang et al., 1997a). As a result, the vegetated channel has a smaller value of t_V than that one with both vegetation and air sparging. The unplanted channel has a smaller mean residence time for horizontal flow and a much larger mean residence time for vertical flow because transport to the atmosphere is reduced compared to channels with vegetation.

The mean residence time values from bromide experiments are much lower than those estimated for water from the model. This reveals that the actual groundwater flow within the saturated zone is preferential instead of uniform. In other words, most of the groundwater flows through a small region of the saturated zone. This small region is most likely that part near the channel bottom, because the water inlets and outlets are at 2 cm above the channel bottom.

Assuming that bromide movement represents the groundwater, the active volume, V_a, can be estimated by:

$$V_a = t_{Br^-} \frac{V_{sat.}}{\tau_H} \tag{22}$$

The remaining portion of saturated zone is inactive. The inactive or dead zone volume, V_d, is:

$$V_d = V_{sat.} - V_a = V_{sat.} \left(1 - \frac{t_{Br^-}}{\tau_H} \right) \tag{23}$$

The dead zone volume and its ratio to the total saturated zone volume are listed in Table 4. The data show that the dead zones in the experimental soil channels occupy a large portion of the saturated zones. The active zone is about 20 cm^2 in cross section, extending the length of the channel.

Results of bromide and TCE recovery from five channels are presented in Table 5. Since only a portion of the bromide was recovered, it is clear that there is slow exchange with some or all of the inactive volume.

More TCE was recovered from groundwater effluent than from the gas phase. When plants are not present, more of the water leaves as liquid and the fraction of bromide and TCE leaving in the liquid effluent is larger. As shown in Table 5 and Figure 8, more TCE is released at the soil surface with air

sparging and plant growth. Higher recoveries of TCE in evapotranspiration effluents of vegetated channels resulted mainly from larger evapotranspiration rates of these channels than the unplanted one. However, the air-sparged channels 1 and 6 have evapotranspiration rates lower than those of channels 2 and 5 which are vegetated but not air-sparged. This is because, for the air sparged channels 1 and 6, the plant growth was reduced during the period from about the thirty-fifth day to the 100th day after TCE injection and starting air sparging. In this period, the detected soil gas TCE and DCE concentrations from channels 1 and 6 were higher than from channels 2 and 5, and the air sparged channels' monthly evapotranspired water amounts were less than 50% of those before the TCE injection.

The pore-water velocity through the inactive zone is small relative to that through the active zone; diffusion and/or dispersion may control TCE transport in the inactive zone. Once TCE reaches the unsaturated zone, it can move by gas diffusion, which is much faster than liquid diffusion. Increasing TCE concentration in the inactive zone, for example, through air sparging, will increase the fraction of TCE transported to the soil surface. The upward flow of gas and the convective motion associated with gas flow affect the upward transport of TCE.

The results in Table 5 suggest that there is some flow along the bottom of each channel with some mixing with the fluid that is associated with the inactive volume. Since there is upward flow due to evapotranspiration, most of the bromide that is lost into the inactive volume appears to move away from the bottom of the channel. The fraction of bromide recovered in the groundwater effluent is less than the fraction of water which leaves as groundwater during the bromide test period. However, the fraction of TCE which leaves in the groundwater effluent is larger than the fraction of water which leaves as groundwater. Since the NAPL is expected to find its way to the bottom of each channel, this provides further evidence that some water flows along the bottom of each channel. The significant difference between the bromide and TCE results may be because the NAPL density greatly exceeds the density of water while the bromide solution has a density much closer to that of water.

CONCLUSIONS

Experiments were conducted to examine the movement of groundwater and TCE with vegetation, without vegetation, and with vegetation under air sparging conditions. Due to root water uptake and plant transpiration, vegetation accelerates TCE upward movement. By enhancing mass transfer and TCE dissolution, air sparging increases TCE concentration in both groundwater and gas phases. As a result, air sparging speeds up the washout of TCE.

Comparing experimental data with flow model results reveals that groundwater flows through the channels are, to a large extent, preferential rather than uniform because of the way water is introduced into the channels. A large portion of the saturated zone appears to remain inactive or less active to groundwater flow. Some of the flow appears to be along the bottom of the channels.

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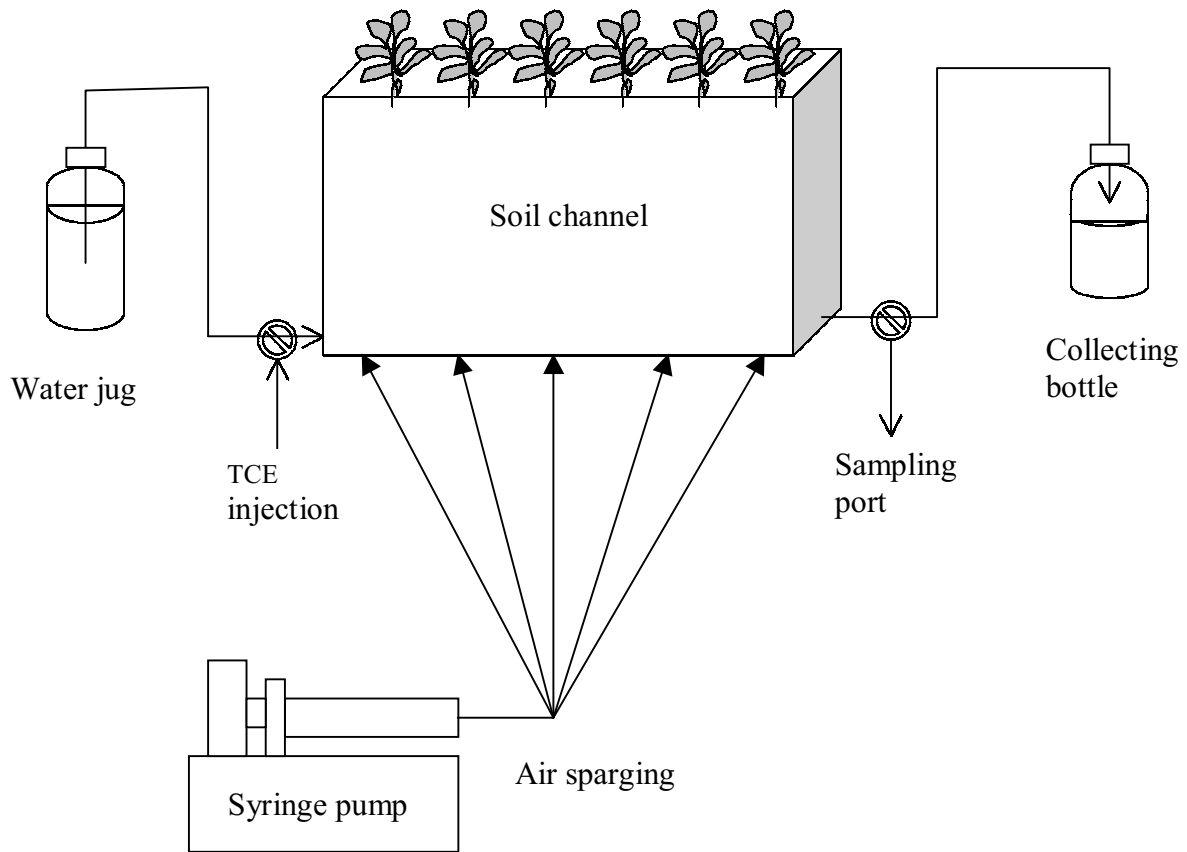**Figure 1.** Schematic diagram of the operating system.
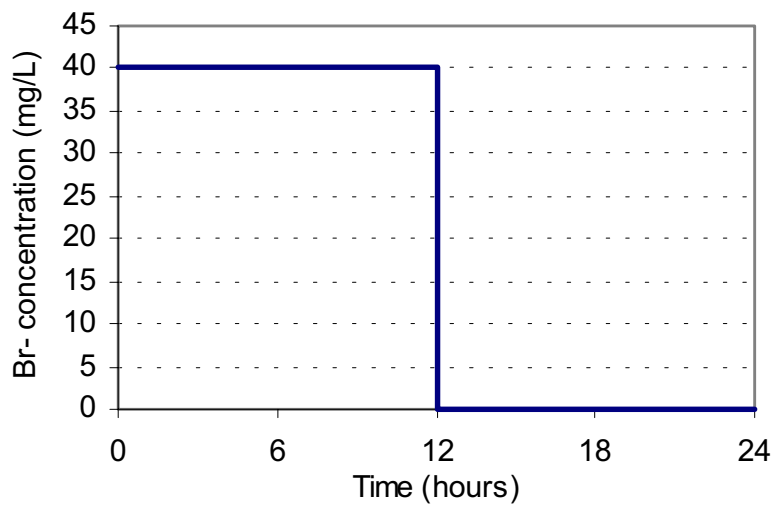

Figure 2. Bromide input function.

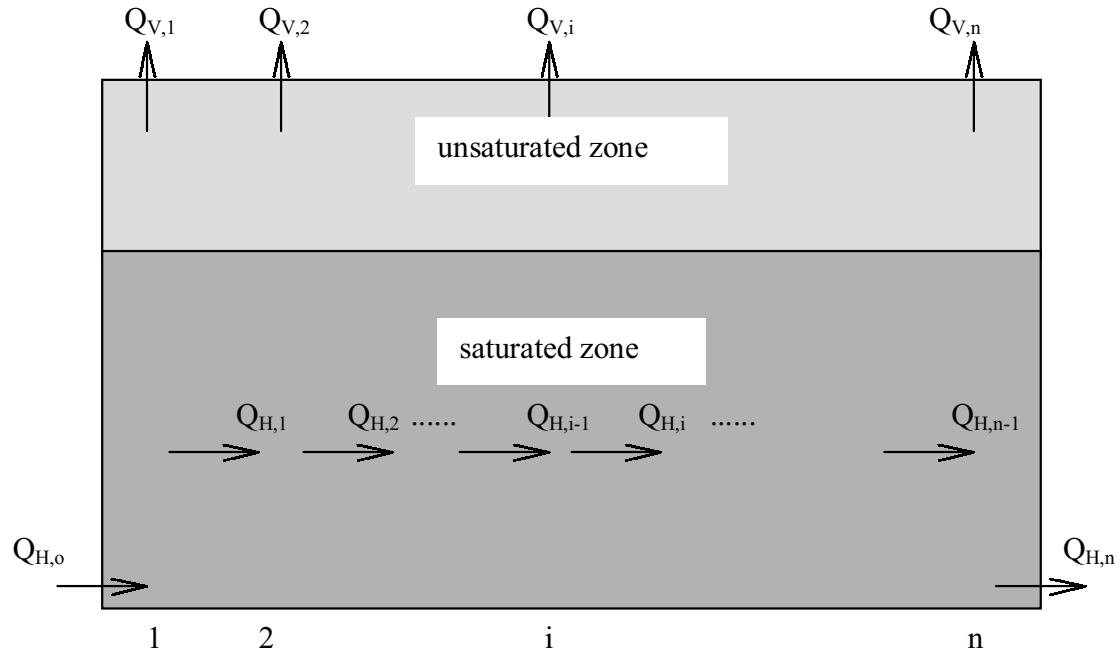**Figure 3.** A schematic diagram of the n-compartment groundwater flow model for a soil channel.

Figure 4. Time records of bromide concentrations in exit stream from channels 2, 4, and 6. There was no air sparging in channel 6 during the bromide tracer test.
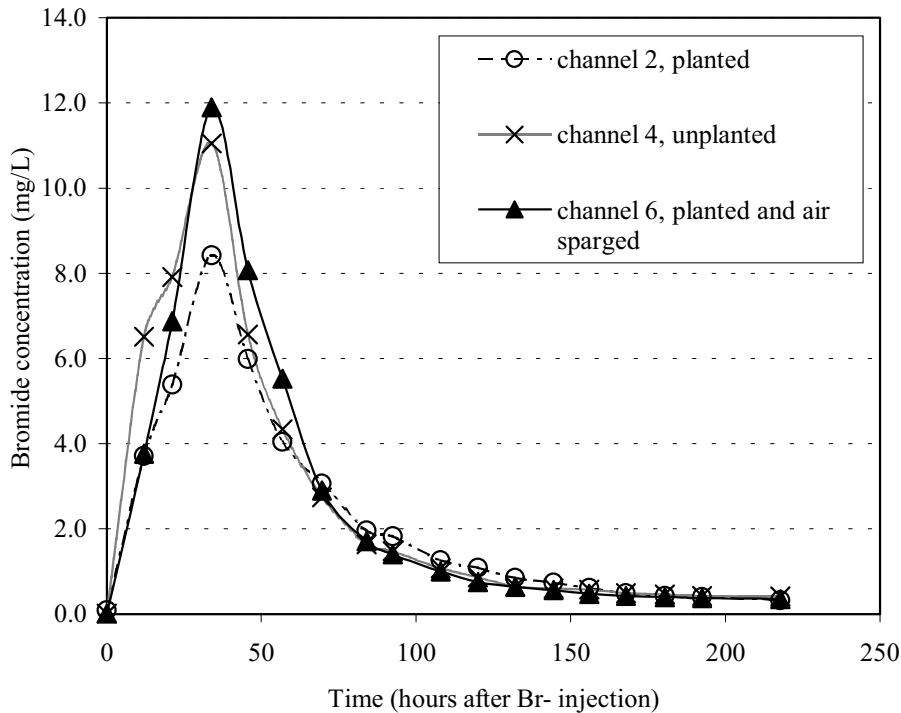
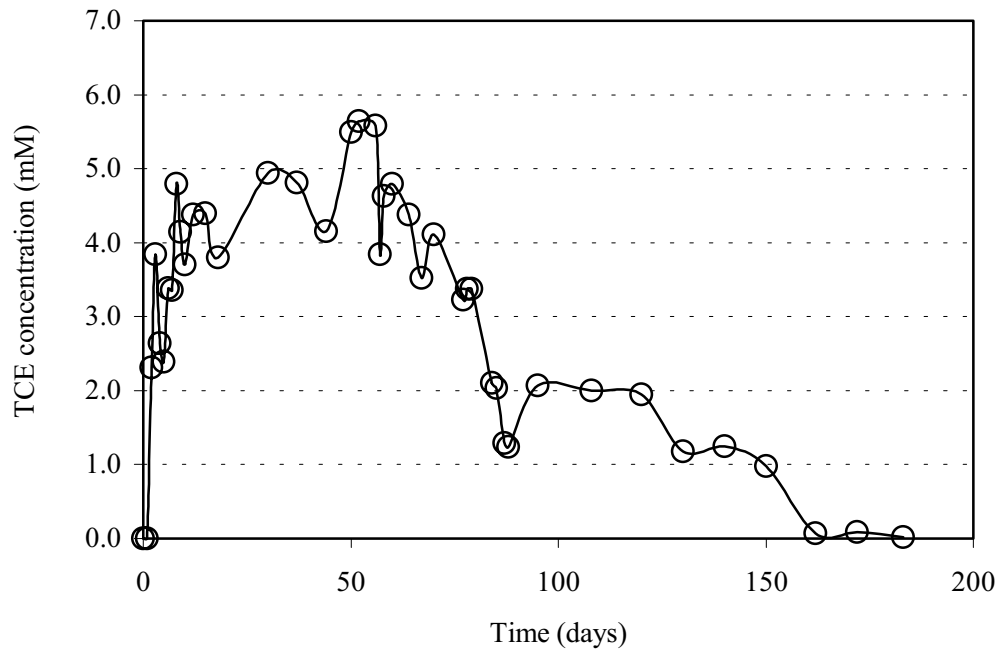**Figure 5.** Time record of aqueous TCE concentration from channel 2 (planted).

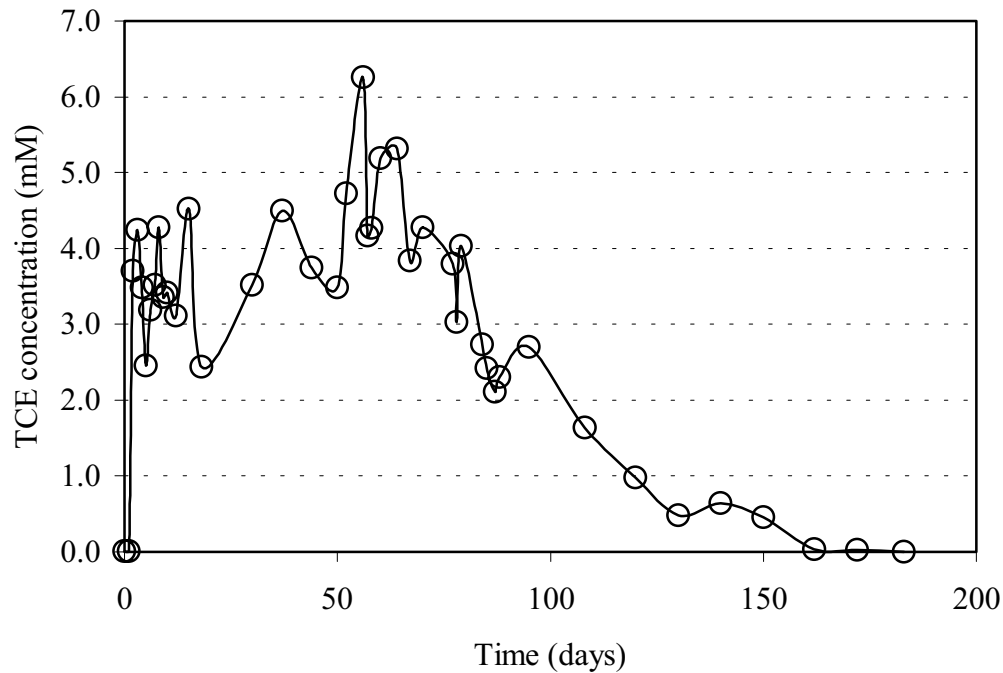**Figure 6.** Time record of aqueous TCE concentration from channel 4 (unplanted.)

Figure 7. Time record of aqueous TCE concentration from channel 6 (planted and air sparged).
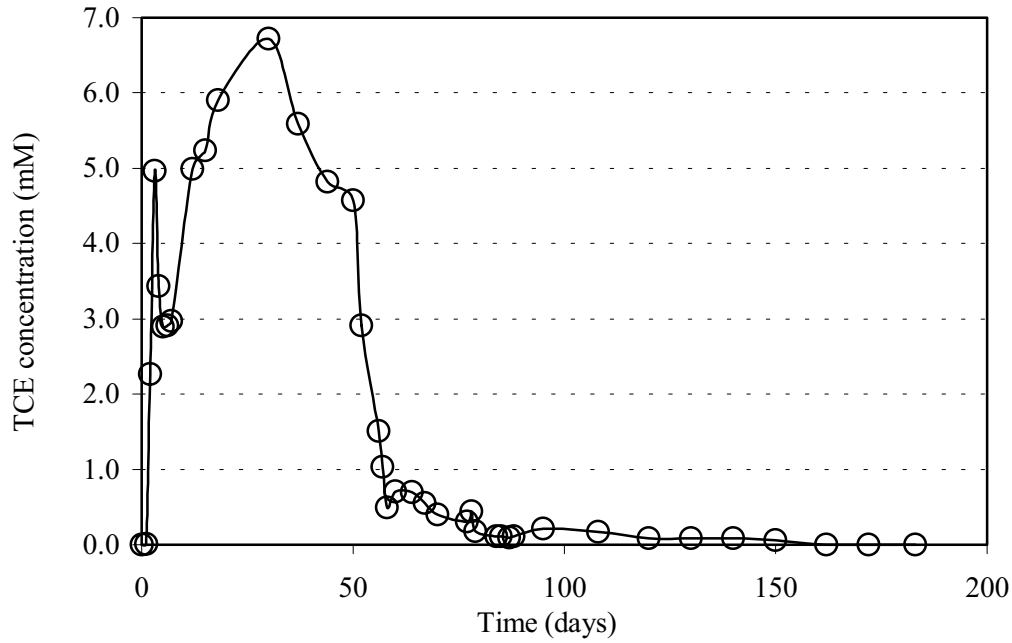

Figure 8. Time record of gaseous TCE concentration from channels 2, 4, and 6.
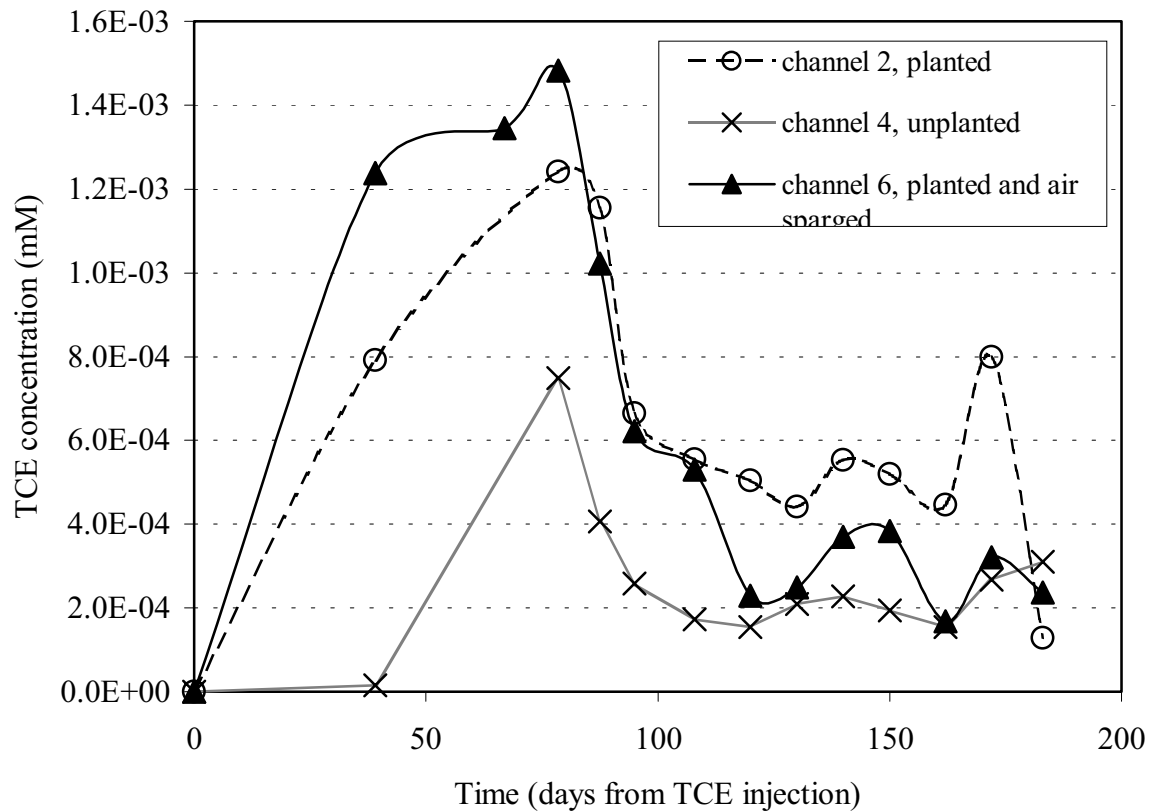
Table 1. Mean residence time (days) of Br and TCE for different channels (experimental results).

channel description	Br⁻ (horizontal)	TCE (horizontal)	TCE(vertical)*
planted	2.32, 2.38	61.3	90.8
unplanted	2.36	58.6	103.1
planted & air sparged		34.4	75.1

*These values are based on the measured values in Figure 8. Measurements were discontinued after more than 150 days when values approached the limit of detection.

Table 2. Mean residence time (days) for water for different values of n (modeling results).

channel description	n = 2		n = 6	
	τ_H	τ_V	τ_H	τ_V
planted	16.7	32.0	17.0	34.7
unplanted	13.3	47.6	13.4	49.9
planted & air sparged	15.8	40.2	15.9	43.2

Table 3. Parameters used to estimate groundwater mean residence time for six-compartment model.

channel description	planted	unplanted	planted & air sparged
$V_{sat.}$ (L)	11.6	11.6	11.6
$V_{unsat.}$ (L)	9.63	9.63	9.63
$Q_{E.T.}$ (L/day)	0.59	0.38	0.45
θ_w (-)	0.80	0.80	0.80

Table 4. Estimated dead zone volumes within saturated zone of channels based on bromide data and the six-compartment model results.

channel description	planted	unplanted	planted & air sparged
V_d (L)	9.85	9.64	9.92
V_d/V_{sat} (%)*	84.9	83.1	85.5

*V_{sat} is assumed to be 11.6 L, so the active zone has volume of less than 2 L.

Table 5. Recovery of bromide, TCE and water for five experimental cases.

channels and descriptions	channel 1 (planted & air sparged)	channel 2 (planted)	channel 4 (unplante-d)	channel 5 (planted)	channel 6 (planted & air sparged)
Fraction of TCE recovered in liquid effluent	0.74	0.85	1.11	1.11	0.71
Fraction of TCE recovered in evapotranspiration effluent	0.18	0.16	0.07	0.12	0.21
Fraction of water recovered in liquid effluent during the TCE experiment	0.41	0.37	0.58	0.40	0.55
Fraction of bromide recovered in liquid effluent	0.074*	0.30	0.49	0.26	0.36*
Fraction of water recovered in liquid effluent during the test period	0.40	0.43	0.54	0.49	0.47

*The bromide test was conducted without air sparging and lasted less than 9 days.