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Experimental and modeling studies of the fate of organic contaminants in the presence of alfalfa plants

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Abstract

Experimental investigations were carried out in the laboratory to study the impact of vegetation in bioremediating soil and groundwater contaminated with hazardous organic substances. A chamber consisting of two U-shaped channels, each 1.8 m in length, 10 cm in width, and 35 cm in depth, was set up. The channels were packed with fine sandy soil collected from near a landfill. Alfalfa plants were grown in the channels under laboratory conditions for nearly two years. The water fed to the plants in one channel was contaminated with toluene solution at saturated concentrations at 26 °C. Plants in the other channel were fed with water contaminated with phenol solution at 500 ppm (v/v). The contaminant concentrations in the groundwater were monitored at sampling wells located along each of the channels. The influent and effluent flow rates from each channel were recorded daily. Evapotranspiration significantly influenced the fate of the pollutants. Dispersion and adsorption processes in the channel were studied separately, by introducing bromide tracer as a broad pulse into the toluene fed channel, and by observing the washout of toluene and phenol contaminants following a feed step change to pure water. Tracer studies indicated that short-circuiting at the U-bend of the channel was quite significant. Previously developed models which described the fate of contaminants in variably-saturated soils in the presence of vegetation are employed to simulate the fate of these hazardous organic substances in the laboratory chamber.

1. Introduction

There is growing body of literature [1–30] which can be applied to investigate the significance of vegetation in the bioremediation of soil and groundwater contaminated with hazardous organic compounds. Vegetation can play a key role in remediating contaminated soil and groundwater by providing a favorable environment

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for biodegradation [1, 2, 6, 8, 11, 12, 17, 22, 24, 29] and controlling the infiltration of landfill leachates and movement of dissolved contaminants [8, 15, 22, 23] near groundwater aquifers.

Biodegradation of many organics occurs in the rhizosphere (root zone of the plants which sustains a genetically diverse variety of microflora) [22, 24, 29]. The roots of the plants exude a wide spectrum of compounds from sugars, amino acids, and carbohydrates to essential vitamins which may act as growth and energy substrates for the microbial consortium in the root zone [7, 23, 24]. Studies by McFarlane et al. [17] showed that the rhizosphere can act as a natural sink for the depletion of atmospheric benzene vapors. Walton and Anderson [29] reported enhanced biodegradation of trichloroethylene (TCE) in the rhizosphere soil as compared to non-vegetated soils without plant roots and associated microflora. More recently, Ferro et al. [11] have shown that establishing crested wheatgrass on PCP-contaminated surface soil may accelerate, by as much as three-fold, the removal of the contaminant.

In the process of bioremediation, vegetation may also take up, translocate or immobilize, and transform some of the organics. The most important parameter of the organics used in research to predict plant uptake from the soil is its octanol–water partition coefficient, K_{ow} (usually, expressed as $\log K_{ow}$) [6]. For barley plants, Briggs et al. [5] studied the uptake of compounds in homologous series but with varied octanol–water partition coefficients. They found that compounds with partition coefficient values of about 100 ($\log K_{ow} = 2$) show a maximum translocation into the transpiration stream of the plant; typically this is as much as 80% of soil-water contaminant concentration. They also cited examples of compounds that deviate from the predictive transpiration stream concentration curve. McFarlane et al. [18] showed that classes of compounds with similar K_{ow} values will be taken up differently depending on the plant species tested.

Compounds with low $\log K_{ow}$ values ($\leqslant 1$) are relatively mobile in both the plant xylem and phloem. Compounds with $\log K_{ow}$ values between 1 and 4 (approximately) are generally considered to be xylem mobile and phloem immobile. Compounds with high $\log K_{ow}$ values ($\geqslant 4$) are generally not substantially translocated into the plants. It is also suggested that generally, the type of soil, including clays and organic matter content, as well as plant rooting structure relative to the contaminant location, can greatly influence plant uptake of any compound [6]. Additionally, accumulation of some of these organic contaminants, resulting from the uptake and immobilization in plants, could also be phytotoxic. Researchers in the herbicide industry in particular, are extending the degrading capacity of soil microflora to plants by incorporating microbial genes into the plant genomes to tackle this problem.

Evapotranspiration associated with photosynthesis helps plants to draw water up into the vadose zone using solar energy. This solar-driven pumping increases the net upward flux of water through the vadose zone, thus lowering the groundwater table and decreasing the soil–water content in the rhizosphere. This results in increased oxygen transfer by gas-phase diffusion in the soil. More importantly, evapotranspiration also brings dissolved hazardous organics to the vadose zone of the soil for biodegradation in the rhizosphere by the microbial consortia which are supplied with basic nutrients from the plants. The solar-driven pumping may also result in the

Table 1
Characteristic features of toluene and phenol at room temperature (26 °C)

Features	Toluene	Phenol
Solubility[a] (mg/l)	550	80200
Specific gravity[b] (g/cm^3)	0.867	1.06
Vapor pressure[a] (mm)	30	0.38
Log K_{ow}[b]	2.65	1.46
Log K_{oc}[b]	2.18	1.43
Wavelength of max. UV absorbance[c] (nm)	261	273
Established conditions for biodegradation	Aerobic and anaerobic (denitrifying and methanogenic)	Aerobic and anaerobic (denitrifying and methanogenic)

[a] From Refs. [20,30].
[b] From Refs. [14,19].
[c] From Ref. [21].

translocation of the organic pollutants into the plant. Boersma et al. [4] showed that accumulation of bromacil in plants increased in proportion to the transpiration rate.

In summary, the plant and associated rhizosphere act as an active in situ bioreactor. The vadose zone of the soil (also the root zone) is a relatively favorable environment for growth of microbial populations and transformation of contaminants for two essential reasons: (a) at the plant roots there is a continuous supply of basic nutrients such as C, N, and P for microbial growth because of fixation and exudation processes; and (b) there is a relatively higher diffusivity of atmospheric oxygen into the soil as a result of the removal of water by the evapotranspiration process.

The plant and associated root system may also act as a pathway for the diffusion of oxygen to the rhizosphere microflora [24]. Under aerobic conditions, the active microbial consortia present in the rhizosphere may biodegrade the organic contaminants before they can be taken up and translocated into the plant. Moreover, plants may help in the biotransformation of dissolved contaminants that may be taken up from the contaminated soil [1, 22, 23, 25].

This research was undertaken to investigate the potential of indigenous rhizosphere microbial consortia to biodegrade organics such as toluene and phenol in the presence of alfalfa plants growing under laboratory conditions. Toluene and phenol are categorized as priority pollutants by the US EPA. Toluene is also classified as a volatile organic contaminant (VOC). The significant features of these two contaminants are listed in Table 1. The principal objectives of this project were: (a) to experimentally study the ability of the indigenous rhizosphere population in bioremediating soil and groundwater contaminated with hazardous organic contaminants such as toluene and phenol; (b) to investigate the response of bromide tracer and study the dispersion and adsorption characteristics in the experimental set-up in the presence of transpiring alfalfa plants; and (c) to compare the experimental observations such as tracer studies, contaminant degradation and washout,

and water content with the previously developed model equations [8, 16, 26] so that the model could be extended further for use in practical situations.

2. Procedures

2.1. Experimental study

A laboratory chamber was constructed with two identical U-shaped channels each 10 cm in width, 1.8 m in length, and 35 cm in depth (see Figs. 1 and 2). The channels were packed with sandy soil (silt $< 10\%$) collected from near a landfill. Alfalfa plants were established in the soil under laboratory conditions. Water that was continuously fed to the plants was contaminated with toluene at its saturated concentration (at 26 °C) in one channel and with phenol (93%) at 0.5 ml/l concentration in the other. Groundwater was sampled at four wells located along the axial length of the channels. Fig. 2 shows the overhead view of the laboratory chamber with alfalfa plants, sampling ports, inlets, and outlets. Fig. 1 shows the frontal view of the laboratory chamber when it is imagined to be axially extended. More details regarding this experimental set-up were previously published in Davis et al. [9] and Erickson et al. [10].

Groundwater concentrations of toluene and phenol were regularly monitored at the inlets, sampling ports, and the outlets for more than one year during the operation of the system. The contaminants in the groundwater were partitioned into an organic phase before measuring their concentrations. Toluene in toluene-contaminated

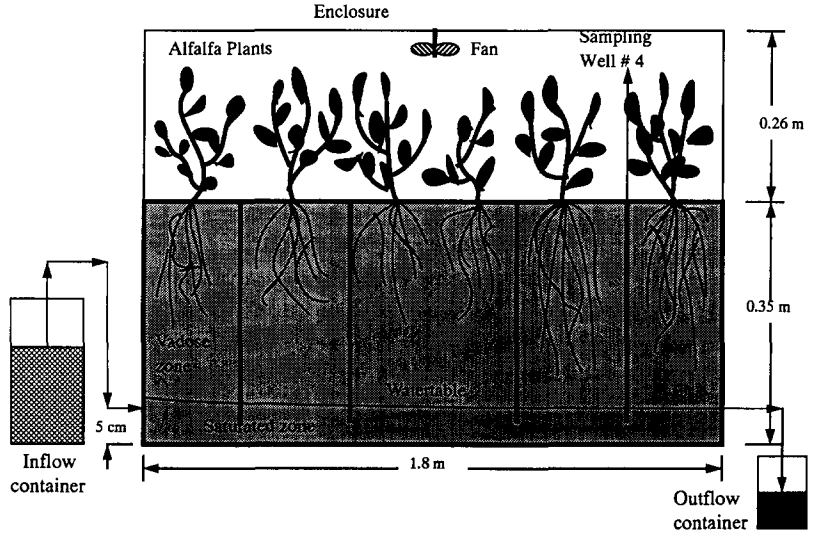

Fig. 1. Schematic view of the axially extended experimental set-up; the actual chamber is 0.9 m long as shown in Fig. 2.

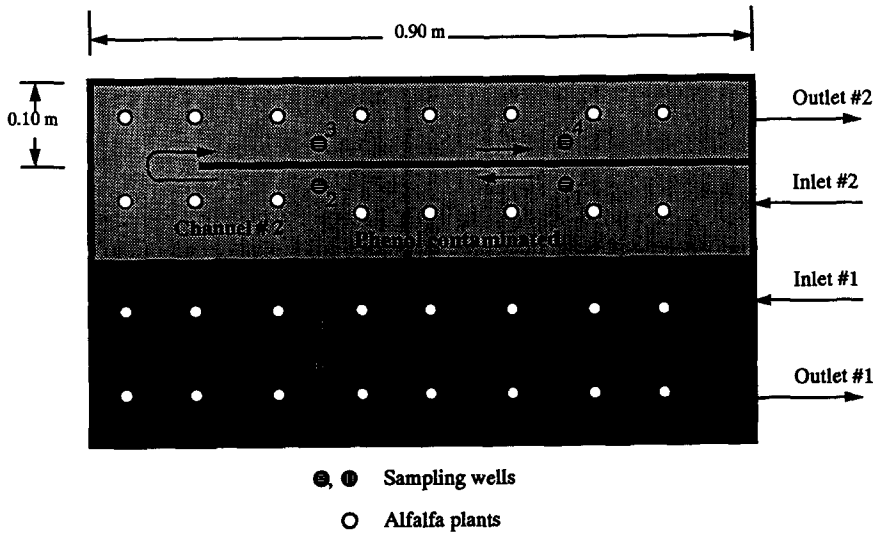

Fig. 2. Overhead view of the actual experimental unit.

groundwater was extracted using three parts of *n*-heptane, by vortexing a mixture of the groundwater sample with *n*-heptane at a ratio of 1:3. Phenol-contaminated groundwater samples were initially treated with 0.1 *M* phosphate buffer (pH = 7) to ensure that phenol remained un-ionized. Partitioning of phenol was performed with *n*-octanol also in the ratio of 1:3. The extracted concentrations of toluene in *n*-heptane and phenol in *n*-octanol were estimated by recording the UV absorbance value using a DU-2 UV spectrophotometer at wavelengths 261 and 265 nm, respectively. Standard extractions were performed for toluene and phenol to calculate the concentrations of the contaminants in the groundwater of the chamber. Occasionally, the entire UV spectrum of the sample in the region 200–300 nm was scanned using a Hitachi model U-3210 recording spectrophotometer.

Toluene is a fairly volatile organic contaminant as compared to phenol. Headspace measurements of the enclosed chamber were performed using a MIDAC Fourier transform infra red (FT-IR) instrument to detect toluene that was either evaporated through the soil pathway or transpired through the plant pathway [9]. Carbon dioxide evolution into the headspace of the chamber from the rhizosphere soils was also measured using the FT-IR spectrophotometer [9].

2.2. *Water content measurements*

Soil samples were collected after more than one year of operation of the system. A 30 cm long and 2 cm diameter hollow plunger with a trap facility at one end was used to collect soil samples from the toluene channel. Samples were obtained from three different locations and at three different depths from each location along the channel. After weighing, the soil samples were dried in an oven at 105 °C for 5 days

and weighed again to determine the dry weight of the samples. The values of gravimetric water content for the different core samples were then calculated.

2.3. Tracer study

Bromide tracer studies were conducted by feeding 6 l of KBr solution to the toluene channel at a concentration of 150 mg of KBr/l from the inflow container shown in Fig. 1. The bromide tracer was input as a broad pulse for a period of 204 h. The concentration of bromide in the groundwater samples was measured regularly using an ion chromatograph. Daily influent and effluent flow rates of water were also recorded during the tracer experiment for over a month.

2.4. Washout study

After about one year of feeding toluene and phenol, the adsorption characteristics of the contaminants in the fine sandy soil in the presence of growing alfalfa plants were studied by making a step change in the inflow groundwater concentration. Pure distilled water was introduced as inflow to both the channels of the chamber. The concentrations of the contaminants in their respective channels were measured regularly during the washout experiments using the previously described measurement technique.

2.5. Modeling study

A variably saturated contaminant degradation model describing the fate of a contaminant in the root zone of actively transpiring plants and associated microorganisms was previously developed [8]. In the model, the biodegradation of the contaminant was assumed to be primarily an aerobic process with limitations on the growth of biomass because of the concentrations of oxygen and organics. The exudation of the sloughed root masses is also considered in the model. Transport of the contaminant is considered in both the horizontal and vertical directions in the aqueous and gas phases of the root-soil environment. The model also considers the gas-phase diffusion of oxygen in the vadose zone of the soil.

The degradation kinetics are assumed to follow a two-substrate Monod kinetic model [3, 8]. Adsorption of the contaminants, root exudates, and biomass onto the soil-particle surfaces and root surfaces is assumed to follow a linear adsorption isotherm. The plant uptake parameter T_{SCF}, was calculated using an empirical relation developed by Briggs et al. [5] and values of $\log K_{ow}$ available in literature (see Table 1). The model equations are published with greater detail in Davis et al. [8], Tracy et al. [27, 28] and Shimp et al. [24].

A transient root-soil water flow model describing the soil-water flux, root-water flux, and soil-water content distribution was developed earlier [16, 26–28]. This model predicts the movement of water in the root and soil phases of actively growing plants. The root parameters used in this simulation were based on the data estimated

from other field and laboratory studies for specific plants growing at specific locations [8, 16, 26]. The soil characteristic parameters used were procured from other earlier laboratory experiments and mathematical relationships [27, 28]. Mathematical relationships describing the soil-water flux (Darcy's law) and soil-water content as a function of the hydraulic conductivity and soil-water pressure head distribution are used.

The root-soil water flow model and variably saturated contaminant degradation models are solved simultaneously using a Galerkin finite element method that employs linear elements and a Crank–Nicholson difference method for approximating the time derivative.

For modeling the bromide tracer experiment the equations in Davis et al. [8] were modified to account only for convective and dispersive transport of the tracer in the presence of transpiring alfalfa plants in the channel. The equations employed in simulating the tracer movement are shown below with all symbols retaining their same original description as published earlier in Davis et al. [8].

$$\frac{\partial}{\partial t}[C(\theta)] = \frac{\partial}{\partial x}\left[\theta\left(D_{xx}\frac{\partial C}{\partial x} + D_{xz}\frac{\partial C}{\partial z}\right) - V_x C\right] + \frac{\partial}{\partial z}\left[\theta\left(D_{zx}\frac{\partial C}{\partial x} + D_{zz}\frac{\partial C}{\partial z}\right) - V_z C\right], \tag{1}$$

V_x and V_z represent the advective flux of water in the soil and are determined using Darcy's law in which the soil-water pressure head distribution is determined using Eqs. (2) and (3).

$$\frac{\partial}{\partial x}\left[K_{sx}\frac{\partial}{\partial x}(\psi_s)\right] + \frac{\partial}{\partial z}\left[K_{sz}\frac{\partial}{\partial z}(\psi_s + z)\right] - q = \left[\beta S_s + S_y\frac{dS_e}{d\psi_s}\right]\frac{\partial \psi_s}{\partial t} \tag{2}$$

$$\frac{\partial}{\partial x}\left[K_{rx}\frac{\partial}{\partial x}(\psi_r)\right] + \frac{\partial}{\partial z}\left[K_{rz}\frac{\partial}{\partial z}(\psi_r + z)\right] + q = R_d\frac{\partial}{\partial t}WC_r + WC_r\frac{\partial R_d}{\partial t}. \tag{3}$$

3. Results and discussion

3.1. Tracer results

Six liters of KBr at a concentration of 150 mg of KBr/l were fed from the inflow reservoir (Fig. 1). Table 2 shows the mass balance for the bromide tracer introduced into the channel. During the whole tracer experiment the average water loss was about 87% of the inflow water. Water loss from the channel was primarily due to transpiration by alfalfa plants. The percentage of bromide tracer retained in the channel was about 81% of the input (425 mg). The amount of bromide retained in the channel was calculated as the difference between the amounts of bromide in the inflow and outflow. The percentage of bromide tracer retained in the channel is directly

Table 2
Mass balance for bromide in the groundwater of the chamber

Bromide inflow conc. (mg/l)	Inflow bromide (mg)	Outflow bromide (mg)	Bromide retained (mg)	Percentage of bromide retained	Percentage of water lost
87.5	525.0	100.0	425.0	81.0	87.0

influenced by the percentage of water lost to the atmosphere. The percentage of bromide that flowed out of the channel was low (only 19%) compared to the percentage retained (81%) in the channel. The vertical movement of water due to evapotranspiration increased the net bromide transport flux into the vadose zone of the soil. This reveals the significance of actively transpiring plants. The higher the ability of alfalfa plants to draw water up from the saturated zone, due to water pressure gradients, the lower will be the amount of bromide flowing out of the channel. Bromide tracer studies indicated that in the presence of actively transpiring alfalfa plants a conservative solute appears at the outlet after about 225 h from the time of its introduction at the inlet of the channel (Fig. 3(c)).

Modeling the tracer transport along the channel was performed using Eqs. (1)–(3). All plant related parameters and soil characteristic parameters were based on previous field, other laboratory, and literature studies [8, 27, 28]. Figs. 3(a)–(c) show the comparison between the experimental and modeling studies for bromide tracer at various locations along the channel. The early sharp discontinuity in the curves was due to plugging at the channel inlet in the beginning part of the tracer experiment. The discontinuity feature was also taken into account during the modeling studies. Fig. 3(b) shows an offset of the simulated curve as compared to experimental data. Comparing Figs. 3(a) and (b), it is clear that the experimental trailing edge results are less time-dispersed (narrower) than predicted by the model. This is primarily attributed to the short-circuiting caused after the U-bend of the channel (Fig. 2).

The model is rather sensitive to evapotranspiration rate because with sufficiently high evapotranspiration rates, there is no net outflow and tracer may take infinite time to arrive at the outlet. Arrival times at the ports are likewise influenced by the evapotranspiration rates. If one models the flow assuming the shortest path between the sampling ports rather than the center-line path of the flow channel, a better fit is observed for the data at ports 3 and 4. The center-line path is about 22 cm longer than the shortest path at the U-bend of the channel.

Flow heterogeneities induced by the U-bend may account for both the steeper experimental data than simulated concentration peaks at ports 3 and 4, and the longer times of the simulated elution graphs as compared to experimental profiles. Arrival time at any port depends on both distance and net flow over that distance. Limitations in precise estimation of the relative evapotranspiration rates along different sections of the channel may also have contributed to the slight differences in the trailing part of the tracer experiment.

3.2. Contaminant degradation

Alfalfa plants growing in each channel were exposed to either toluene or phenol for more than one year. Toluene solution at its saturated concentration (at 26 °C) was fed to the groundwater from the inflow container into channel No. 1 and phenol solution at a concentration of 0.5 ml of 93% phenol per liter of water ($\approx$ 500 mg/l) was fed to the groundwater to channel No. 2 (Figs. 1 and 2). It was assumed that with contaminants fed continuously at such high concentrations, the system reached a steady state in about four months from the start of the experiment. By steady state, we mean

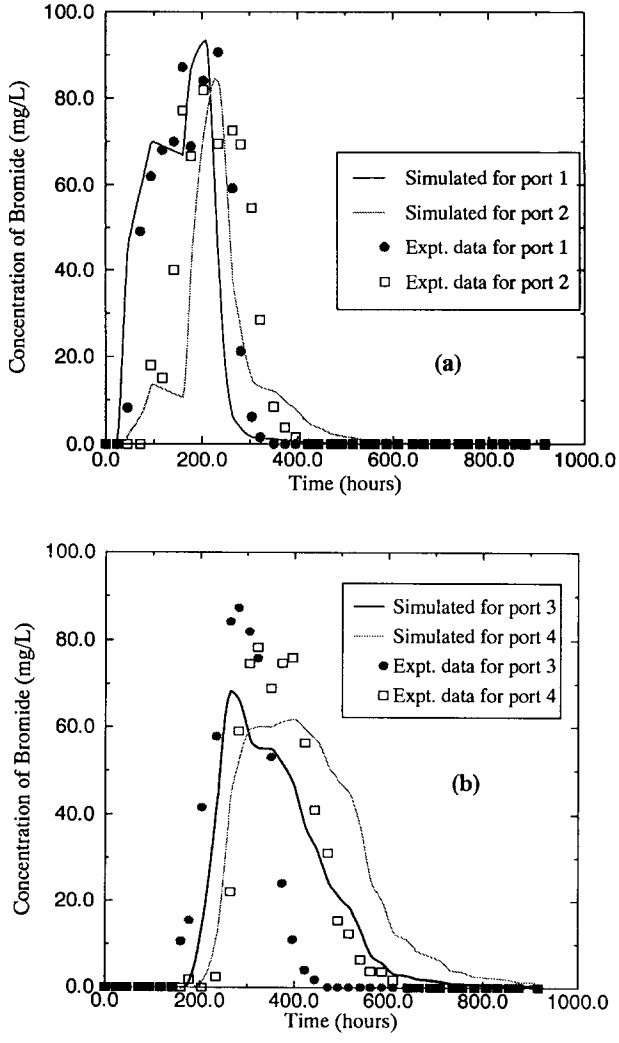

Fig. 3. Comparison of simulated and experimental values for bromide tracer at (a) port 1 and port 2, (b) port 3 and port 4, (c) outlet.

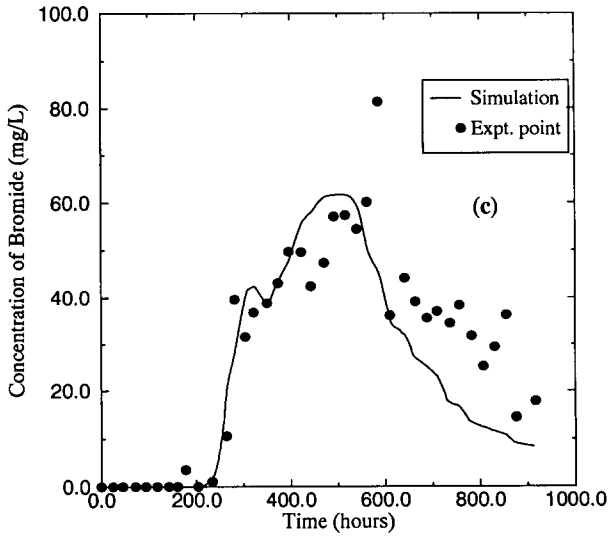

Fig. 3. Continued.

Table 3
Concentrations in mg/l of toluene and phenol in the groundwater during the steady-state operation in the chamber

Compound	Inlet	Port 1	Port 2	Port 3	Port 4	Outlet
$C_6H_5CH_3$[a] (Toluene)	497.9 ± 34.5	434.4 ± 48.9	417.7 ± 60.6	420.8 ± 61.6	403.1 ± 77.3	455.2 ± 55.3
C_6H_5OH[b] (Phenol)	497.4 ± 32.3	456.7 ± 43.9	367.5 ± 43.5	164.0 ± 18.6	31.5 ± 17.0	23.6 ± 11.9

[a]All values are mean concentrations ± SD in mg/l ($n > 10$).
[b]Mean concentrations ± SD of 5 groundwater samples.

that adsorbed concentrations reached constant values, the biodegradation rates of the contaminants and growth rates of the microbes reached a plateau, and all transpiring plants became well-adapted to growth in the presence of the contaminants.

Table 3 shows the concentrations of toluene and phenol measured along the axial length of the channel. The mean and standard deviations of the steady-state measurements for toluene were obtained after collecting more than ten samples of groundwater from the channel. The toluene and phenol groundwater samples were collected from different periods of time (spread over 3 months) during the steady-state operation of the experiment. It can be observed from Table 3 that the error was only about 10–15% in the groundwater concentration measurements. This error could be either associated to the non-periodic contaminant additions as inflow into the channel or

Table 4
Amount of toluene and phenol in the inflow and outflow groundwater during the steady-state period of operation

Compound	Inflow conc. (mg/l)	Volume of inflow (ml/day)	Outflow conc. (mg/l)	Volume of outflow (ml/day)	Percentage of compound lost	Percentage of water lost
$C_6H_5CH_3$ (Toluene)	497.9	900	455.2	240	76.0	73.0
C_6H_5OH (Phenol)	497.4	850	23.6	250	99.0	71.0

Table 5
Mass balance for contaminant carbon, mmol/day

Compound	Inflow carbon (mmol)	Outflow carbon (mmol)	Carbon disappearing (mmol)
$C_6H_5CH_3$ (Toluene)	34.0	8.2	25.8
C_6H_5OH (Phenol)	27.0	0.3	26.7

due to the flow heterogeneities in the channel soil. The concentration of toluene at various port locations remained approximately uniform along the length of the channel and constant over the steady-state period of operation. In other words, spatial (along the axial length) and temporal variations in toluene concentration were minimal. The concentration of toluene in the sampling wells was lower as compared to the inlet and outlet concentrations. These consistently low values may be due to the volatilization of toluene to the headspace of the closed but not sealed sampling wells or due to biodegradation of toluene in presence of atmospheric oxygen available in the headspace of the well.

Phenol concentration decreased drastically along the 1.8 m long channel. This decline (prominent after port 2 of the phenol channel) was evident after about eight months from the start of the experiment and was less during the earlier operation. The large drop in concentration is attributed to anaerobic degradation that occurred in addition to the already established aerobic biodegradation in the vadose zone (also the rhizosphere) of the channel.

Table 4 shows the mass balances for both the contaminants in the groundwater during the steady-state operation of the system. About 76% of inflow toluene and 99% of inflow phenol were lost. The corresponding water usage in each channel was 73% and 71%, respectively. The results in Table 4 can be used to estimate the amount of carbon that disappears each day; this is given in Table 5.

At room temperature, the vapor pressure of toluene is about 30 mm and that of water is about 25 mm. The driving force for volatilization is larger for toluene as compared to water because water is usually present at a fraction of saturation in the

atmosphere. Therefore, a parallelism in the disappearance of toluene and water from the groundwater is not surprising. Phenol is relatively non-volatile (vapor pressure <1 mm, see Table 1); the significant loss of phenol is attributed to aerobic and anaerobic biodegradation. The relative extent of loss of phenol due to anaerobic biodegradation was not quantified.

Fourier transform infra red (FT-IR) headspace measurements of the chamber showed that gas-phase concentrations of both of these contaminants were below the limits for detection of the instrument. The limits for detection of the instrument varied from 250 ppb (v/v) to 1 ppm (v/v) depending on the day of measurement [9]. Based on the inlet concentrations, this is the amount that would be released into the atmosphere of the enclosed chamber along with approximately 1 ml of water transpired or evaporated. About 10 ml of water was transpired per hour, per channel [31].

The concentration of toluene remained constant in the saturated zone. For this volatile contaminant, the concentration driving force would favor the vertical movement of toluene contaminant from the saturated zone across the vadose zone of the channel. However there was no measurable toluene appearing in the headspace of the chamber even after 18 h of equilibration [9]. This indicated that the vadose zone which contained indigenous mixed microbial consortia contributed to the loss of toluene that was transported in the vertical direction. The rhizosphere is a favorable habitat for the growth of a genetically diverse microbial population. Nutrients such as N and P, are either fixed at the plant roots [24] or supplied in the form of exudates to the microbes [7]. It is also possible to have comparatively higher oxygen diffusivity in this soil zone due to the decrease in soil–water content caused by evapotranspiration. Clearly, the rhizosphere plays the key role as an active bioreactor by sustaining a diverse microbial population which supplies enzymes that catalyze the aerobic biodegradation of toluene.

Phenol is relatively less volatile. Hence, evaporation losses of phenol are minimal. Transpirational losses may be dependent on the capacity of the transpiring alfalfa plants. However, this pathway for the loss of phenol was also measured and found to be minimal. The same argument that was true for aerobic toluene biodegradation may also be extended to explain the disappearance of phenol in the vadose zone. Self-stimulated anaerobic degradation of phenol was observed in addition to the expected aerobic biodegradation.

Occasionally, UV spectra of groundwater samples from each of the channels were compared to that of their respective standards. The UV spectra of the samples always matched well with their corresponding standard spectra. This indicated the absence of any stable dissolved intermediates of biodegradation from either of the contaminants.

3.3. CO_2 estimation

The results of FT-IR measurements undertaken to detect the CO_2 evolution into the headspace of the chamber are shown in Table 6. It was observed that on the average about 85 mmol of CO_2/day evolved from the well-adapted transpiring alfalfa plants' root zone when contaminants were fed to the chamber. When all of the contaminants were washed out from the system, an average of about 57 mmol of

Table 6
FT-IR estimates of CO_2 transport into the headspace of the chamber (mmol/day)

CO_2 with contaminant feed (mmol)	CO_2 without contaminant feed (mmol)	CO_2 due to contaminant degradation (mmol)
85.0	57.0	28.0

Table 7
Significant modeling parameters used during the simulation of toluene (at 26 °C)

Microbial parameters	
Maximum specific growth rate	0.1/h
Endogenous metabolism rate	0.001/h
Soil parameters	
Porosity	0.35
Bulk density	1.5 g/cm^3
Toluene parameters	
Monod saturation constant	50.0 mg/l
Soil adsorption coefficient	0.375 cm^3/g
Root concentration factor	4.135
Transpiration stream concentration factor	0.575
Dimensionless Henry's law constant[a]	0.274
Effective vadose zone gas-phase diffusivity[a]	3.25×10^{-4} m^2/h
Oxygen parameters	
Monod saturation constant	8.0 mg/l
Dimensionless Henry's law constant[b]	37.5
Effective vadose zone gas-phase diffusivity[b]	7.42×10^{-4} m^2/h

[a] from Refs. [30, 13].
[b] from Ref. [20].

CO_2/day was observed. This suggested that about 28 mmol of CO_2/day evolved from the complete aerobic biodegradation of about 52 mmol of carbon fed per day in the form of the contaminants (see Table 5). This also suggests a carbon yield factor of about 0.5 for biomass formation from the contaminant degradation.

3.4. Modeling results

The steady-state operation of the system was modeled for both the contaminants. As the model [8, 27, 28] considers only the aerobic degradation of contaminants in the rhizosphere, the comparison of experimental data with simulation results was not attempted for phenol. Some of the parameters used in modeling toluene degradation in the rhizosphere are shown in Table 7.

Fig. 4 shows the steady-state simulated concentration profiles for toluene at various depths of the channel. It is important to notice that the simulated toluene

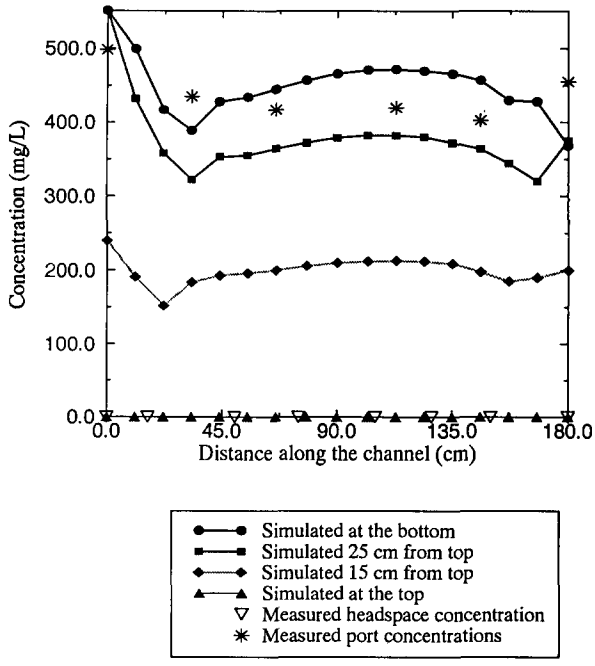

Fig. 4. Simulated concentration profiles of toluene during steady-state operation at different depths in the channel.

concentration remained approximately constant at the bottom along the length of the channel during the simulation. This is consistent with the experimental data represented in Table 3. Also, the toluene concentration progressively decreased in the rhizosphere bioreactor from the bottom to the top of the channel where it approached a concentration of 0 ppm. This is consistent with the FT-IR measurements of the headspace of the enclosed chamber [9]. It is therefore clear from Fig. 4 that toluene disappeared in the rhizosphere of the plant growing chamber and this disappearance is attributed to the aerobic degradation of toluene by the indigenous microbes.

The parameter sensitivity for the model was examined. The Monod saturation constants for toluene and oxygen represented in Table 8, were found to have large effects on the simulated curves. Changing the saturation constant by ten-fold gives a distinctly poorer fit with the observed data. The maximum specific growth rate of the biomass, gas phase diffusivity of toluene and oxygen, and adsorption coefficient onto the soil-particle surface were other parameters tested to study the sensitivity of the model. The maximum specific growth rate of the biomass had an appreciable effect on the simulation. A 10% change in maximum specific growth rate of biomass significantly affected the steady-state concentration of toluene in the channel. It was also observed that when the simulation was run with a zero maximum specific growth rate for the microorganisms, the system became completely saturated with toluene from the bottom to the surface of the channel.

Table 8
Gravimetric water content values measured along the channel expressed as grams of water/gram of dry soil

Chamber depth (cm)	Distance along the length of the channel from the inlet (cm)		
	20	80	160
0–10	0.186	0.179	0.178
10–20	0.222	0.231	0.211
20–30	0.231	0.243	0.222

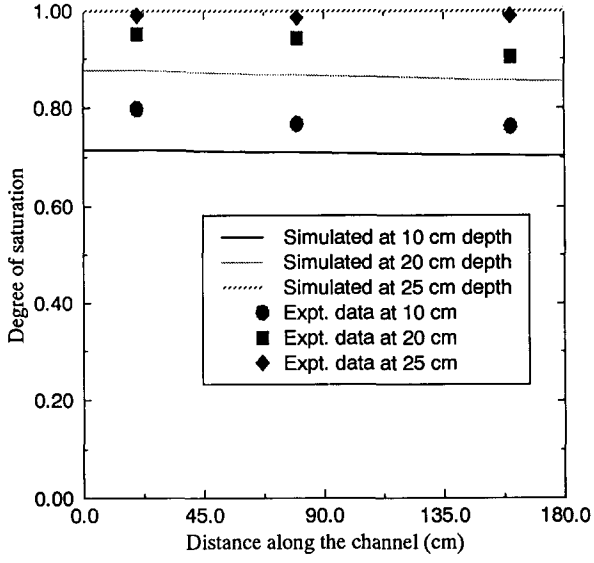

Fig. 5. Comparison of simulated and measured values for degree of saturation at different depths along the axial length of the channel.

Modest changes in the gas-phase diffusivity of oxygen from the atmosphere had a less appreciable effect on the simulation results. Aerobic biodegradation occurs at a reasonable rate as long as oxygen and the contaminant are present. Oxygen is transported downward while the toluene is transported upward; biodegradation occurs where both are present. The soil-water content in the vadose zone of this shallow system was relatively high (Fig. 5). It was observed that the soil-water content was as much as 70% saturated in the surface of the channel (Fig. 5). This is possible for a shallow system with actively transpiring plants. Usually, the capillary zone extends to about 25–40 cm above the groundwater table for fine sandy soil. This may be even higher with the evapotranspiration process actively moving water to the surface of the soil. Since the water-phase diffusivity of oxygen is 10000 times smaller than the

gas-phase diffusivity, one would expect the effective diffusivity to be significantly less than the tabulated literature gas-phase diffusivity when the soil is relatively wet. The simulation results in Fig. 4 were obtained with a gas-phase diffusivity for oxygen which is about 100 times smaller than the literature value [20].

These results indicate that with actively transpiring plants in a relatively shallow system, it is plausible to completely biodegrade toluene and phenol. Also, the results reveal the significant role of vegetation in biodegrading toluene and phenol which were fed at relatively high concentrations. It must be emphasized that lack of replication of this experimental set-up with transpiring alfalfa plants may tend to limit the implications of these results to actual field situations. Nevertheless, the potential for vegetative bioremediation to deplete dissolved organic contaminants in the rhizosphere soil is feasible in relatively less humid states, like Kansas, where evapotranspiration usually exceeds the overall annual precipitation [27, 28].

3.5. *Water content results*

Table 8 shows the gravimetric water content values at the various locations of the channel. It was observed that with a porosity of 0.35 and bulk density of 1.5 g/cm^3, the degree of saturation in our system varied from about 70% near the surface to about 99% near the groundwater table. This indicates the degree of wetness in the surface soil of such a shallow chamber with an actively transpiring alfalfa plant system. Usually, in practical field situations, a greater depth of the groundwater table generally limits the wetness in soil with transpiring plants as compared to our laboratory scale situation. Fig. 5 shows the simulated values for the degree of saturation as compared to the corresponding measured values in the system. There is reasonable agreement between the simulated and experimental values.

3.6. *Washout of toluene*

Figs. 6(a)–(c) show that there is a small difference between the modeling and experimental results for the washout of toluene following a feed step change to pure water. The model considers dispersive phenomena, plant uptake, biodegradation, and adsorption–desorption during the washout simulation. The parameter values which are given in Tables 1 and 7 are the same as those used to simulate the steady-state performance of the system.

During the setup of the experimental system it was determined that the organic carbon content (f_{oc}) was about 0.3% in the bottom soil of the toluene channel. It was found that the value of soil-adsorption coefficient had an appreciable effect on the simulation of washout of toluene from the channel. The soil-adsorption coefficient (K_{ds}) in Table 7 was calculated based on Eq. (4).

$$K_{ds} = f_{oc} K_{oc}. \tag{4}$$

For the simulation, organic matter content (f_{oc}) was taken to be 0.25% at the bottom of the toluene channel. This gave a reasonably good fit with the observed washout data (Figs. 6(a)–(c)).

Bromide tracer washout began at 204 h after the introduction of bromide tracer. Thus, the bromide tracer elution graphs are not directly comparable with the washout of toluene. Since the average flow rates to the channel were the same after the beginning of the washout experiment for either solute, comparison could be made

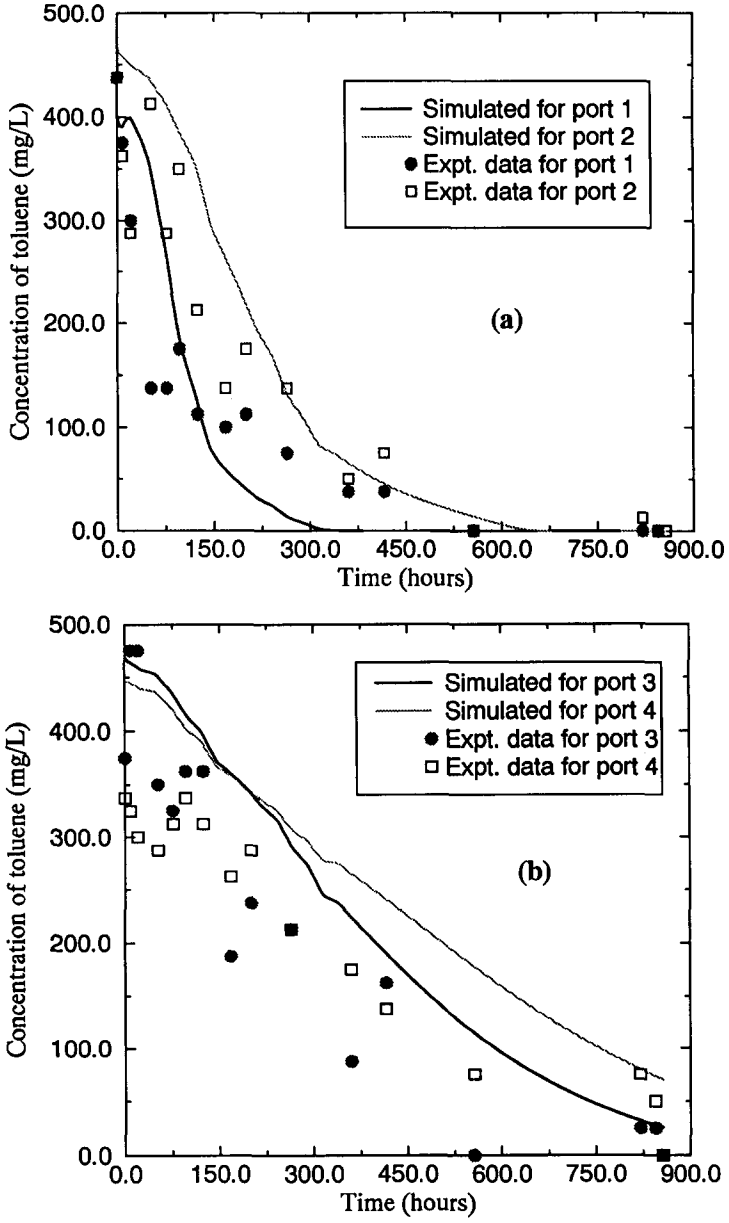

Fig. 6. Comparison of simulated and experimental values during the washout of toluene at (a) port 1 and port 2, (b) port 3 and port 4, (c) outlet.

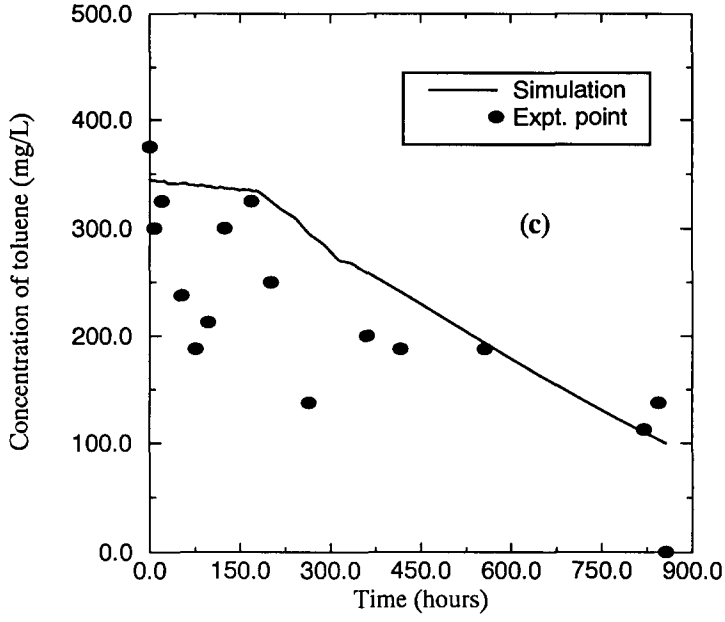

Fig. 6. Continued.

after simply displacing the tracer trailing edge by 204 hours. Running the toluene washout simulation without including adsorption gives a significantly lesser extent of trailing. These comparisons show that adsorption onto the soil is an important process for toluene transport through the chamber. As with the KBr tracer experiment, a better fit for the later ports is obtained if a shortest path rather than the channel center-line distance is used for the interval between ports 2 and 3.

4. Summary and conclusions

The rhizosphere of well-adapted actively transpiring alfalfa plants may act as a self-sustaining bioreactor that supports the growth of a genetically diverse mixed microbial consortia. These indigenous microbes with the provision of growth substrates and nutrients, such as C, N, P, and O_2, are capable of biodegrading many contaminants. Vegetation plays an additional role by transpiring large volumes of water. The associated dissolved contaminants are carried up into the vadose zone with the water and consequently biodegraded by the active microbial population in the rhizosphere. The microbial biodegradation rates may be far higher than the uptake and transformation rates by the plant biomass so that the accumulation of the contaminants in plants may not be of concern. Contaminants may also be biotransformed by plant biomass subsequent to their uptake and accumulation from contaminated soils.

Contaminant concentrations in the gas phase were measured and found to be below the detection limit. Less than 1% of the contaminants are lost to the gas phase.

The observed experimental results are in good agreement with those predicted by a mathematical model which includes evapotranspiration, plant uptake, biodegradation, adsorption, oxygen transfer, and microbial growth.

Finally, alfalfa plants are capable of growing in laboratory conditions even when relatively high concentrations of toluene and phenol are fed continuously for long periods of time.

Nomenclature

C	concentration of the tracer in aqueous phase (g/m^3)
D_{ij}	dispersion coefficient (m^2/h)
$K_{si,ri}$	hydraulic conductivity of soil and root, respectively, in the ith direction (m/h)
q	plant uptake of water (m/h)
R_d	root density (m^3/m^3) (dimensionless)
S_e	effective degree of saturation (m^3/m^3) (dimensionless)
S_s	specific storativity (1/m)
S_y	specific yield (m^3/m^3) (dimensionless)
t	time (h)
V_i	convective volumetric flux in the ith direction (m/h)
WC_r	root-water content (m^3/m^3) (dimensionless)
x, z	Cartesian coordinates (m) (axial and vertical directions, respectively)

Greek letters

β	$= 0$ if $\psi_s \leqslant 0$ and
β	$= 1$ if $\psi_s > 0$
θ	volumetric soil-water content (m^3/m^3) (dimensionless)
$\psi_{s,r}$	soil-water and root-water pressure head (m)

Subscripts

i, j {for $i, j = x, z$}	spatial index
r	root
s	soil

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