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Transport and biodegradation of toluene in unsaturated soil

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Abstract

Degradation of volatile organic chemicals during transport has received little attention in the past. In this study we report the results of a series of experiments on toluene movement through soil columns of different length in sterilized, pre-exposed and unexposed soil. Toluene was added to 25-cm-diameter soil columns through an inlet chamber that maintained a constant concentration throughout the experiment. The toluene diffused through the soil to an outlet chamber at the top which was continuously swept with humidified air and samples were periodically analysed to determine toluene flux. The first experiment, conducted under sterilized conditions, was used to measure the soil gas diffusion coefficient, and subsequent experiments in which biodegradation occurred were used to estimate the degradation rate coefficient by fitting the outflow to a mathematical model. The degradation rate was very rapid under both pre-exposed and unexposed soil conditions, corresponding to a half-life of ~ 2 h when bacterial activity reached high levels. Prior to this stage, the volatilization flux was very erratic, implying that growth rates of the bacteria were out of phase with the transport process. Overall, the degradation process was not well described by a first-order model until the population stabilized. Pre-exposure of the soil to the substrate prior to the transport experiment greatly increased the rate of removal of toluene during transport. Under such conditions, a 30-cm cover could virtually stop volatilization losses of the compound when the inlet concentration was well below saturation, and could decrease it by a factor of $\geqslant 30$ even when the inlet concentration was saturated.

1. Introduction

Volatile organic chemicals (VOC's) can be introduced into the subsurface environment in a variety of ways, such as from leaking underground storage tanks, land disposal sites, accidental spills and agricultural applications. Besides their potential for contaminating groundwater, VOC's may volatilize into the atmosphere, thereby

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creating a potential health threat to individuals living in the vicinity of the emission sources (Glotfelty et al., 1987; Karimi et al., 1987).

Capping the surface with a fine-textured, compacted soil is a common practice to prevent chemical volatilization from landfills and abandoned waste disposal sites. The effectiveness of a soil cover at reducing or eliminating volatile emissions depends on both the soil properties and the properties of the chemical of interest. Jury et al. (1990) used a chemical screening model to evaluate losses of 35 organic chemicals through different types of soil cover, and were able to calculate a limiting cover thickness required to reduce volatilization to insignificant levels. Their model assumed that the compound underwent first-order degradation during its passage through the cover by diffusion, so that its application required knowledge of the VOC soil diffusion and degradation rate coefficients.

The kinetics of biodegradation reactions have been described by a variety of mathematical expressions, increasing in complexity as they attempt to accommodate the numerous variables that can affect the biodegradation rate in the natural environment. Some VOC transport models do not include biodegradation at all (Falta et al., 1989; Mendoza and Frind, 1990; Brusseau, 1991; Gierke et al., 1992), while others use simplified representations such as first-order reaction kinetics (Jury et al., 1983, 1990; Frind et al., 1990), or Michaelis–Menten kinetics (Molz et al., 1986; Widdowson et al., 1988; Chen et al., 1992). First-order reactions, which assume a constant biomass, are normally observed in short incubation studies conducted at low chemical concentrations. When microbial growth is involved and biomass is produced, the biodegradation reaction rate is better described by the Michaelis–Menten equation which assumes that the test chemical is the single growth-limiting substrate in the system. However, this assumption is unlikely to be true in the natural environment because microbial growth may also result from other substrates which may or may not be growth-limiting (Battersby, 1990).

Experimental information on the degradation of VOC's in soil is very limited. Only the model by Chen et al. (1992) has been tested in well-controlled laboratory column experiments, where reasonable agreement was found. A host of problems, such as modeling microbial growth, representing degradation in different phases, and identifying diffusive limits to microbial breakdown of compounds, need to be solved before the transport and degradation problem can be simulated quantitatively (Jury, 1994).

With these problems in mind, we conducted a series of experiments to measure and model the simultaneous transport and degradation of toluene in large laboratory soil columns. In this paper, we examine the effect of microbial degradation on toluene movement through unsaturated soil under different toluene concentrations and soil conditions, test the validity of the first-order degradation model, and test the validity of existing models for gas diffusion through soil.

2. Theory

The mathematical model used to design experiments and to evaluate the results in this study was a modified form of the behavior assessment screening model published by Jury et al. (1983). The model was developed based on the following assumptions: (1) diffusion is the dominant transport process; (2) the sorbed and the dissolved phases undergo reversible, linear equilibrium sorption; (3) the dissolved and gaseous phases obey Henry's law; (4) the biodegradation reactions obey first-order kinetics; and (5) the soil diffusion coefficients for the gaseous and dissolved phases are modified from their values in air and water by tortuosity factors described by the model of Millington and Quirk (1961):

$$\xi_g = a^{10/3}/\phi^2 \tag{1a}$$

$$\xi_l = \theta^{10/3}/\phi^2 \tag{1b}$$

where ξ_g and ξ_l are the vapor and liquid tortuosity factors, respectively; a is volumetric air content; θ is volumetric water content; and $\phi = a + \theta$ is the total soil porosity.

With these assumptions the chemical transport equation may be expressed in terms of the gas-phase concentration as:

$$R_g \frac{\partial C_g}{\partial t} = D_{soil} \frac{\partial^2 C_g}{\partial z^2} - \mu_{soil} C_g \tag{2}$$

where R_g, D_{soil} and μ_{soil} are defined as follows:

$$R_g = (\rho_b K_d + \theta + \alpha K_H)/K_H \tag{3}$$

$$D_{soil} = (\xi_g K_H D_g^a + \xi_l D_l^w)/K_H \tag{4}$$

$$\mu_{soil} = (\rho_b K_d \mu_a + \theta \mu_l)/K_H \tag{5}$$

where ρ_b is the soil bulk density (g cm^{-3}); C_g is the gas concentration within the soil air phase (mg cm^{-3}); K_H is the dimensionless form of Henry's constant; K_d is the distribution coefficient (cm^3 g^{-1}) between the dissolved and sorbed phases; D_g^a and D_l^w are the binary diffusion coefficients of the chemical in air and water, respectively; and μ_a and μ_l are the first-order decay constants in the sorbed and dissolved phases, respectively.

The experimental apparatus used for measuring gas flow in our study had a constant lower boundary condition and an approximately zero upper boundary condition. Thus, Eq. 2 was solved subject to the following initial and boundary conditions:

$$C_g(0, t) = C_0 \tag{6a}$$

$$C_g(L, t) = 0 \tag{6b}$$

$$C_g(z, 0) = 0 \text{ or } C_0 \tag{6c}$$

For the case where the soil was sterilized prior to the gas transport experiment, Eq. 2 is solved with $\mu_{soil} = 0$, subject to Eq. 6 and the nonzero initial condition. This solution is given by (Carslaw and Jaeger, 1959):

$$C_{\rm g}(z,t) = C_0\left[\sum_{N=0}^{\infty}\left\{\operatorname{erfc}\left(\frac{R_{\rm g}(2NL+z)}{2(R_{\rm g}D_{\rm soil}t)^{1/2}}\right)\right.\right.$$
$$\left.\left.-\operatorname{erfc}\left(\frac{R_{\rm g}[2(N+1)L-z]}{2(R_{\rm g}D_{\rm soil}t)^{1/2}}\right)\right\}\right] \tag{7}$$

$$\operatorname{erfc}(x) = 2\pi^{-1/2}\int_x^{\infty}\exp(-x^2)\mathrm{d}x \tag{8}$$

is the complementary error function.

The corresponding solution for the gas flux leaving the surface at $z = L$ is given by:

$$J_{\rm g}(L,t) = 2C_0\left(\frac{R_{\rm g}D_{\rm soil}}{\pi t}\right)^{1/2}\left[\sum_{N=0}^{\infty}\exp\left(-\frac{R_{\rm g}(2N+1)^2L^2}{D_{\rm soil}t}\right)\right] \tag{9}$$

Eq. 9 may be fitted to the data measured from the upper chamber of the soil column by varying $D_{\rm soil}$ until the agreement between the predicted and measured fluxes is maximized. The fitted $D_{\rm soil}$-value may then be used together with the measured values of a, θ, $\rho_{\rm b}$, $K_{\rm d}$ and $K_{\rm H}$ to check the validity of the Millington–Quirk model (Eq. 1) for the tortuosity factors.

The solution of Eq. 2 subject to Eq. 6 with the zero initial condition for non-sterilized soils (i.e. $\mu_{\rm soil} \neq 0$) at $z = L$ is given by:

$$J_{\rm g}(L,t) = 2C_0\left(\frac{R_{\rm g}D_{\rm soil}}{\pi t}\right)^{1/2}\sum_{N=0}^{\infty}\exp\left[-\frac{R_{\rm g}(2N+1)^2L^2}{4D_{\rm soil}t}-\frac{\mu_{\rm soil}t}{R_{\rm g}}\right]$$
$$+\,C_0(\mu_{\rm soil}D_{\rm soil})^{1/2}\sum_{N=0}^{\infty}\left[\exp\left\{-\left(\frac{\mu_{\rm soil}}{D_{\rm soil}}\right)^{1/2}(2N+1)L\right\}\right.$$
$$\times\operatorname{erfc}\left\{\frac{R_{\rm g}(2N+1)L}{2(R_{\rm g}D_{\rm soil}t)^{1/2}}-\left(\frac{\mu_{\rm soil}t}{R_{\rm g}}\right)^{1/2}\right\}-\exp\left\{\left(\frac{\mu_{\rm soil}}{D_{\rm soil}}\right)^{1/2}(2N+1)L\right\}$$
$$\left.\times\operatorname{erfc}\left\{\frac{R_{\rm g}(2N+1)L}{2(R_{\rm g}D_{\rm soil}t)^{1/2}}+\frac{\mu_{\rm soil}t}{Rg}\right\}\right] \tag{10}$$

When $D_{\rm soil}$ is known then the data can be used to evaluate $\mu_{\rm soil}$ at any point in time. Thus, if the microbial population density increases after the chemical is introduced, the apparent $\mu_{\rm soil}$ for the system will be time-dependent.

3. Materials and methods

3.1. Soil characteristics and preparation

The soil used in this study was a Pachappa loam (coarse-loamy, mixed, thermic

Mollic Haploxeralfs) containing ~ 0.49% organic C which was collected from the experiment station of the U.S. Salinity Laboratory in Riverside, California, U.S.A. The site was not known to have been exposed to toluene before. The soil was air-dried, passed through a 2-mm sieve and throughly mixed prior to use.

For the toluene transport experiments, volumetric soil water contents ranging from 0.08 to 0.15 cm^3 cm^{-3} were prepared by spraying a known amount of water onto a given amount of soil. The moist soil was thoroughly mixed and equilibrated in double plastic bags for at least 24 h before being packed into columns.

3.2. Chemical properties

Toluene was selected for the study because it is typical of compounds most frequently emitted from land disposal sites and it is not likely to induce density-driven flows even at high concentrations (Falta et al., 1989). It has a relatively high Henry's constant $K_H = 0.28$ and an organic C partition coefficient K_{oc} of 155 cm^3 g^{-1}.

3.3. Experimental apparatus

Fig. 1 shows the details of the flow system that was used to study toluene vapor transport through a soil cover. This apparatus was modified from the volatilization cell described by Karimi et al. (1987). It consisted of a bottom chamber, a soil column and an upper chamber which were all constructed of aluminum in order to resist corrosion. Both the bottom and the upper chambers were 30 cm wide, 30 cm long and 7 cm deep. The soil column was 25 cm in diameter, and of variable length (20 or

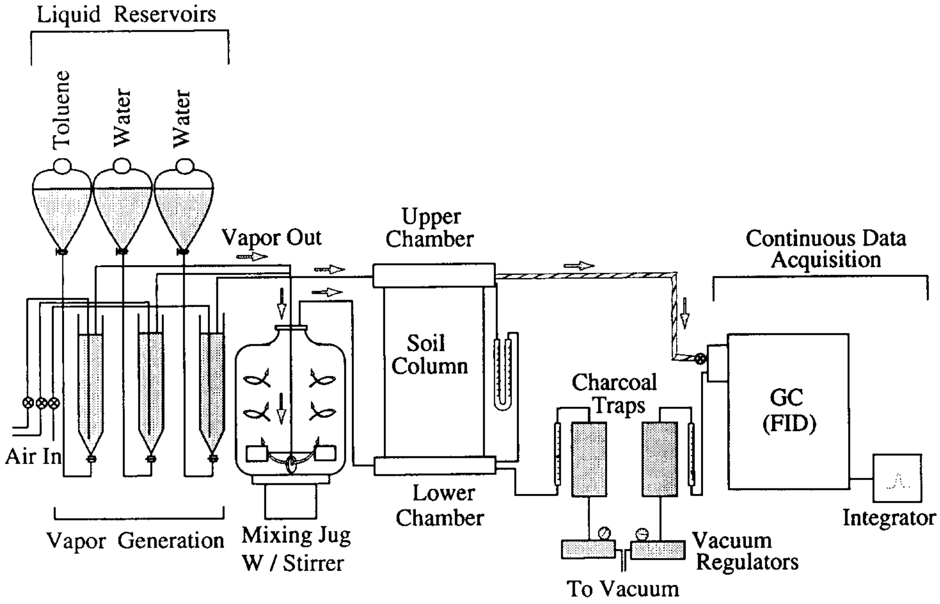

Fig. 1. Schematic diagram of the volatilization cell and flow system used in vapor transport experiments.

40 cm) to represent different thicknesses of soil covers. Volatilization cells used in previous studies (Spencer and Cliath, 1979; Farmer et al., 1980; Karimi et al., 1987) could only operate with saturated vapor at the source by injecting liquid waste into the bottom chamber.

Our system was adapted to handle subsaturated vapor concentrations by adding a dilution system prior to the introduction of the chemical vapor into the volatilization cell. Saturated toluene vapor and humidified air were first generated by passing air through toluene and water tubes, respectively, and then the saturated toluene vapor was diluted by the humidified air in the mixing device. The desired toluene concentration was obtained by adjusting the two flow rates. A second humidified air stream was used to sweep the upper flux chamber and to carry any volatilized toluene to a gas chromatograph (GC) for analysis. Humidified air streams were used to prevent soil in the column from drying during the experiments. The system was automated with an on-line GC and was programmed to sample at 15-, 30- or 60-min intervals. Two charcoal traps were used to absorb the toluene exiting from both the upper and bottom chambers. A water-filled manometer was added between the upper and the bottom chambers to monitor any pressure differences in the system.

3.4. Analytical procedures

Toluene samples were analyzed by a Varian® *1400* GC with a flame ionization detector (FID) containing a 0.5 mm × 30 m megabore column with the bound phase DB-WAX® (J & W Scientific, Folson, California, U.S.A.) at a film thickness of 1 μm. Sample sizes varied between 0.5 and 1.0 mL, depending on toluene concentration. The injector temperature and the oven temperature were both set at 90°C, while the FID temperature was maintained at 250°C. Nitrogen was used as the carrier gas and detector make-up gas at flow rates of 10 and 20 mL min^{-1}, respectively. The hydrogen flow rate was 30 mL min^{-1} and the air flow rate was 400 mL min^{-1}. A Hewlett Packard® *3396*A integrator was used for data acquisition.

3.5. Vapor transport and degradation studies

The toluene diffusion and degradation experiments carried out in this study are summarized in Table 1. In each experiment, soil that was previously equilibrated to a given water content was weighed to yield the desired bulk density and packed into the soil column. Soil water contents were determined at the beginning of the experiments by subsampling from the prepared soil prior to packing. Soil samples were also taken from different depths at the end of the experiments for selected soil columns, and showed no significant variations between water contents measured at the beginning and after the experiments.

The soil was held in place by a fine mesh stainless-steel screen at the bottom of the soil column. For the experiments conducted at saturated toluene concentration (140 mg L^{-1}), liquid toluene was injected into the bottom chamber through a sampling port using a syringe. The amount of toluene added was sufficient to form a liquid layer in the chamber and to supply toluene at the constant saturated concentration for the

Table 1
Summary of variables used in the toluene diffusion and degradation experiments

Expt. No.	Column length (cm)	Water content (cm^3 cm^{-3})	Bulk density (g cm^{-3})	Input C_0 mg L^{-1})	Comments
1	20	0.14	1.33	140.0	sterilized soil[a] (Fig. 2)
2	40	0.15	1.34	11.1	fresh soil[b] (not plotted)
3	20	0.12	1.32	140.0	fresh soil (Fig. 4)
4	20	0.08	1.28	25.1	fresh soil (Fig. 5)
5	20	0.14	1.33	27.6	pre-exposed soil[c] (Fig. 6)
6	40	0.15	1.37	140.0	pre-exposed soil (Fig. 7)

[a] Sterilized soil: soil saturated with toluene vapor for 3 weeks.
[b] Fresh soil: soil never exposed to toluene.
[c] Pre-exposed soil: soil had been used in previous toluene experiment.

duration of each experiment. After placement of toluene, the port was sealed by a screw to prevent leaking. A vapor gap between the toluene layer and the soil surface prevented toluene from migrating by liquid flow through the soil. The air flow rate into the upper chamber was balanced by applying a vacuum to the outlet end at the same rate to prevent pressure changes within the chamber.

For the experiments conducted at lower toluene concentrations ($\ll$ 140 mg L^{-1}), toluene vapor was generated in the dilution system shown in Fig. 1. The flow rate through the bottom chamber was also balanced the same way as for the upper chamber. The system was controlled to prevent pressure gradients, so that no advection occurred and diffusion was the only transport mechanism for toluene. During each experiment, toluene concentrations in the bottom chamber and in the mixing vessel were monitored and found to be constant with time.

The toluene flux from soil surface was calculated from the measured concentrations and the air flow rate from the upper chamber in each experiment.

4. Results

The purpose of expt. *1* was to measure the toluene diffusion coefficient (D_{soil}) for the Pachappa soil used in our study, and to test the validity of the Millington–Quirk tortuosity model (Eq. 1). In this experiment, the soil was sterilized by saturating the soil column and chambers with saturated toluene vapor (140 mg L^{-1}) for a period of 3 weeks, after which the top chamber was swept by the air stream and the flux measured. Fig. 2 shows the comparison of the measured toluene breakthrough curve in the sterilized soil with the flux prediction (Eq. 9) when the Millington–Quirk model Eq. 1 was used. It is clear that the Millington–Quirk tortuosity model underestimates the tortuosity factor, and hence underestimates toluene diffusion through soil. D_{soil}, the diffusion coefficient of toluene through soil, was estimated to be 1580 cm^2 day^{-1} using the Levenberg–Marquardt sum of squares minimization parameter fitting program (Press et al., 1988). In contrast, the calculated D_{soil} from the Millington–Quirk tortuosity model was only 1004 cm^2 day^{-1}. The reported

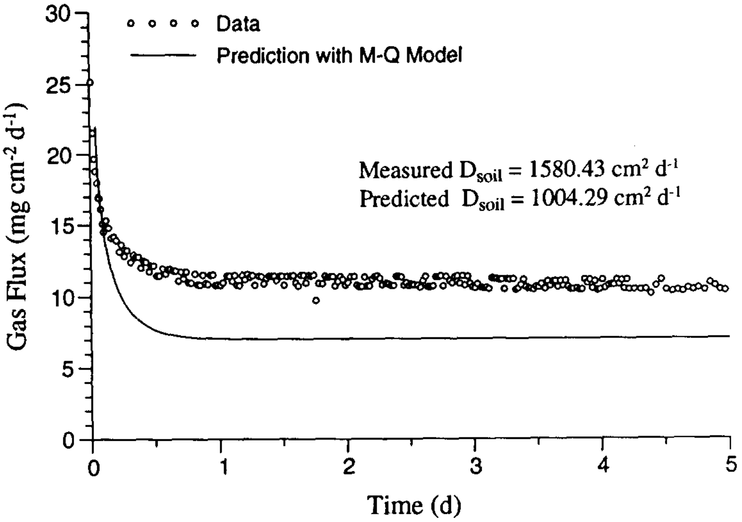

Fig. 2. Comparison of the measured toluene breakthrough curve in a sterilized soil with model prediction when the Millington–Quirk tortuosity model was assumed.

toluene diffusion coefficient of 7258 cm^2 day^{-1} in free air (D_g^a) (Bolz and Tuve, 1970) was used in the above calculations, which is comparable to the value of 6995 cm^2 day^{-1} we calculated by Fuller's equation (Fuller et al., 1966). Thus, the source of disagreement between measured and predicted soil diffusion coefficients is in the tortuosity factor.

We verified this result in a two-chamber diffusion system using an inert tracer, Freon *12*® (CCl_2F_2), which was similar to that used by other researchers (Sallam et al., 1984; Glauz and Rolston, 1989; Voudrias and Li, 1993). Full details of the experimental design and procedures are given in Jin (1994). The D_{soil}/D_g^a ratios measured for Freon® at various soil water contents are plotted in Fig. 3 along with the one point measured for toluene in the previous sterilized soil experiment. The excellent agreement between the toluene and the Freon® data confirms the finding in expt. *1*. Also plotted in Fig. 3 are the Penman model and the Millington–Quirk model. The Penman model ($\xi_g = 0.66a$) is another tortuosity model that has been proposed in the literature (Penman, 1940). The Penman model appears to form an upper limit and the Millington–Quirk model a lower limit for the tortuosity factors in the soil, respectively, at the range of air-filled porosity studied.

The measured tortuosity factor for toluene was used to evaluate the results of the following experiments instead of the Millington–Quirk model predictions.

Experiment *2* was conducted in a fresh soil (i.e. a soil which is not known to have been exposed to toluene previously) at a low toluene concentration (11.1 mg L^{-1}) in the bottom chamber and a zero initial condition. A 40-cm-long soil column was used to represent a relatively deep soil cover. Toluene vapor should have moved through the soil column to the upper chamber within a day based on its diffusion coefficient if there was no loss of chemical en route by degradation reactions. However, no toluene was detected

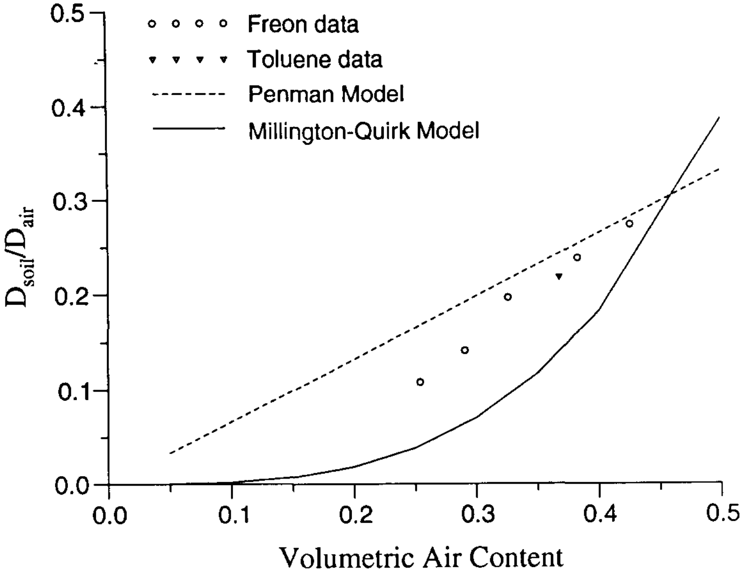

Fig. 3. Comparison of the measured toluene and Freon $12^{®}$ tortuosity factor values with the Millington–Quirk model and the Penman model estimations.

(detection limit: 0.3 mg L^{-1}) in a 6-day period. Apparently, the gas moving through the 40-cm-thick soil cover had a long enough diffusion time that microbial degradation could prevent even low-level toluene vapor from diffusing into the atmosphere.

We proceeded with the next experiment (expt. *3*) using a shorter column (20 cm) and at a saturated toluene concentration (140 mg L^{-1}) in the lower chamber in order to move enough toluene through the soil to study its degradation behavior. This case represents a situation where toluene exists as a concentrated source within the soil (e.g., as a NAPL). The measured toluene breakthrough curve and the model fitted curve are plotted in Fig. 4. The shape of the toluene breakthrough curve was fitted well by the model solution Eq. 10 with the previously measured diffusion coefficient and a first-order degradation rate constant $\mu_{\text{soil}} = 34.2$ day^{-1}. This μ_{soil}-value was estimated by fitting the model to the steady-state part of the outflow curve which is independent of R_g. Then the gas partition factor $R_g = 4.36$ (Eq. 3) was obtained by fitting the model to the entire outflow curve using the measured D_{soil}- and the estimated μ_{soil}-values.

The estimated degradation rate constant 34.2 day^{-1} corresponds to a half-life of ~ 2 h ($t_{1/2} = \ln 2/\mu_{\text{soil}}$) which is significantly shorter than the values reported for toluene in aquatic systems (Howard, 1990), where oxygen is often rate-limiting. The fast rate we measure is more typical of rates observed in a biofilm reactor where aerobic conditions prevail (Archangeli and Arvin, 1992). The toluene flux reaching the outflow end has been reduced by more than a factor of 30 from the amount that would leave the soil if no biodegradation was occurring. The sorption distribution coefficient K_d was calculated to be 0.76 cm^3 g^{-1} from the fitted R_g-value (Eq. 3). The corresponding K_{oc}-value is 155 cm^3 g^{-1} which agrees very well with the reported

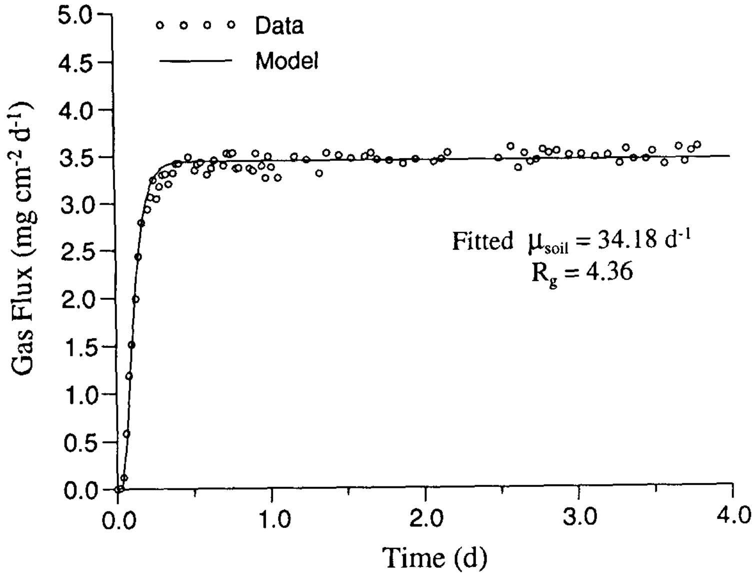

Fig. 4. Toluene breakthrough curve in a fresh soil at saturated toluene concentration (140 mg L^{-1}). The first-order degradation rate constant μ_{soil} and the gas-phase capacity factor were estimated by parameter fitting.

values in the literature (Garbarini and Lion, 1986; Jin and O'Connor, 1990; Jury et al., 1990; Lyman, 1990). We repeated this experiment using a soil sample obtained later from the same site and observed virtually the same result.

Experiment *4* was conducted in a fresh 20-cm-high soil at a lower toluene input concentration of 25.1 mg L^{-1}. Toluene vapor quickly reached the upper chamber and its flux decreased as a function of time in a chaotic pattern and then reached an undetectable level at day 12 (Fig. 5). All experimental variables (temperature, flow rates, etc.) were carefully controlled and the input toluene concentration was monitored and found to be constant during the experiment. We also observed similar fluctuating volatilization over a comparable time period when we repeated the experiment later using fresh soil from the same site. Therefore, we believe that the observed chaotic toluene behavior was not an experimental artifact. The continuous but erratic decrease in toluene flux is probably caused by microbial population growth and/or enhanced microbial activity due to the introduction of toluene. The chaotic behavior could have been caused by the interactions of many processes such as overshooting of microbial population growth, rate-limited diffusion, and possible competition between different microbial species. Clearly, first-order degradation kinetics cannot be used to describe such behavior.

Experiment *5* was performed under identical conditions to that of expt. *4*, except that the soil had been exposed to toluene in a previos experiment. The toluene breakthrough pattern was similar in the two experiments, showing a maximum flux at early times, followed by a nonuniform, erratic decline to an undetectable level. However, the time required to reach an undetectable toluene level was much shorter

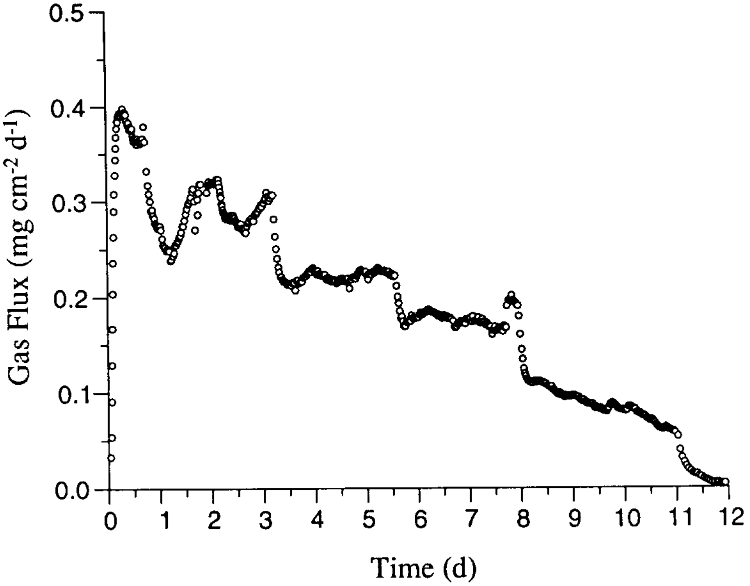

Fig. 5. Toluene breakthrough curve in a fresh soil at low toluene concentration (25.1 mg L^{-1}).

in the pre-exposed soil than in the fresh soil, indicating higher microbial activity in expt. *5* due to the previous exposure of the soil to toluene.

Experiment *6* was conducted in a previously exposed soil but at a saturated toluene input concentration of 140 mg L^{-1}, using a 40-cm-long column. In this case, the toluene outflow curve showed a different pattern than that observed in previous experiments (Fig. 7). The toluene flux reached a high level then quickly dropped after ~ 1 day and approached a steady-state at day 3. There are two possible reasons which could explain such a significant decrease in toluene flux, gravitational stratification of the water or enhanced biodegradation over time. Vertical redistribution of water along the soil column due to gravity could result in an accumulation of water at the lower portion of the column, thereby reducing the diffusion coefficient. However, in a separate study we packed a soil column at the same water content and let it stand vertically for several weeks. When the column was sectioned we found that the water content was uniform throughout the profile. The low water content also facilitates oxygen transport to the degradation sites. Since O_2 is replenished continuously from both the top and the bottom of the column, we think it is unlikely that oxygen supply is limiting the reaction rates in any way. Thus, the toluene flux decrease observed in this experiment is also due to microbial growth or enhanced activity. The time required to reach the steady-state flux in Fig. 7 corresponds to the lag period needed for the microorganisms to adapt to toluene as a primary substrate.

Although the behavior of toluene in this experiment cannot be described by first-order degradation kinetics, a first-order degradation rate constant μ_{soil} can be estimated from the steady-state part of the breakthrough curve for comparison purposes. The μ_{soil} of 42.5 day^{-1} estimated for this pre-exposed soil is higher than

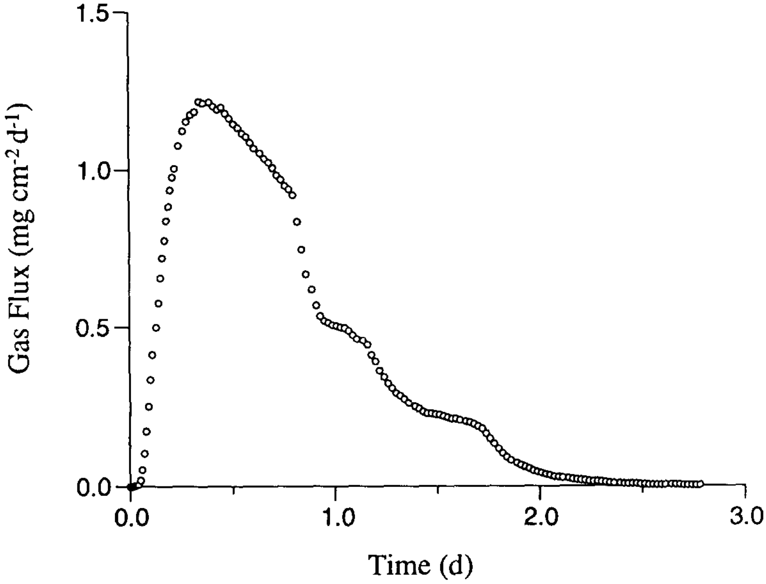

Fig. 6. Toluene breakthrough curve in a previously exposed soil at low toluene concentration (27.6 mg L^{-1}).

that observed for the fresh soil used in expt. *3*. The significant decrease in the steady-state toluene flux in this soil as compared with the flux measured in the fresh soil in expt. *3* (0.1 vs. 3.5 mg cm^2 day^{-1}) is due to the combined effects of increased soil cover thickness and enhanced biodegradation rate.

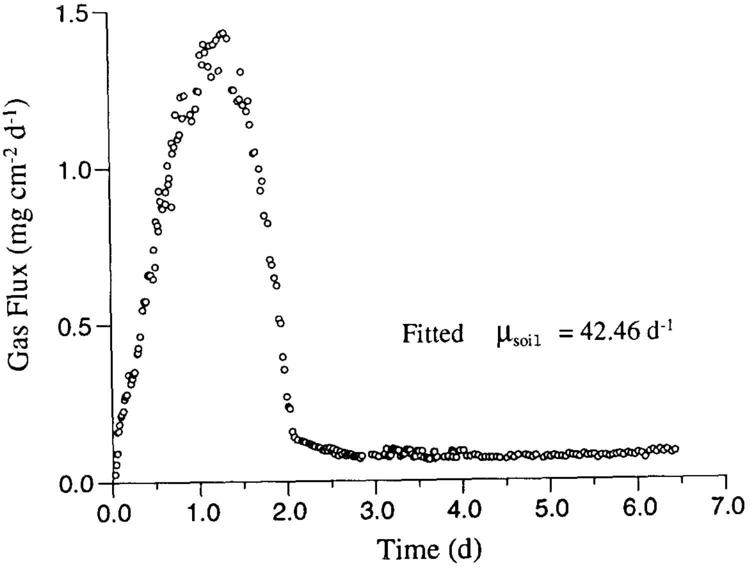

Fig. 7. Toluene breakthrough curves in a previously exposed soil at saturated toluene concentration (140 mg L^{-1}). The first-order degradation rate constant μ_{soil} was estimated by parameter fitting.

5. Discussion

5.1. Rate of toluene biodegradation

Toluene volatilization through soil was significantly reduced at high toluene concentrations (expts. *3* and *6*) and was completely eliminated (expt. *2*) or reached an undetectable level after a lag period (expts. *4* and *5*) at low concentrations due to biodegradation reactions. The remarkably high toluene degradation rates observed in our experiments not only imply that biodegradation is rapid for this compound, but also that the diffusion time into the liquid from the gas phase is not significantly limiting the process. This is consistent with the findings of Schwarzenbach et al. (1993), who used a two-film model to calculate diffusion times on the order of seconds to few minutes for gas molecules to move to the air–water interface, dissolve and move through the liquid films typically found in soil.

5.2. Kinetics of toluene biodegradation

Toluene degradation reaction rates appear to depend on the substrate concentration as well as the history of the soil used. Only for the combination of fresh soil and saturated concentration (Fig. 4) was the behavior of toluene degradation consistent with the first-order kinetics model. However, this does not necessarily indicate a true first-order reaction because only the outflow flux was measured. Rather, it indicates that the overall reaction rates for the entire column were not changing with time.

The results from the other experiments (Figs. 5–7) cannot be described by the first-order kinetics model. While a change in microbial growth/microbial activity is evident in all cases, the different shapes of the toluene outflow curves are probably a consequence of a complex dependence of biodegradation reactions on many factors (e.g., soil condition, substrate concentration, nature of microorganisms). A more complicated model including population dynamics, toxicity effects and other factors would be needed to describe such behavior, and such a model would necessarily contain many parameters that would be difficult to estimate.

5.3. Effect of soil cover thickness

Increasing the soil cover thickness significantly reduced toluene volatilization flux as indicated by expts. *2*, *3* and *6*. The steady-state toluene flux decreased from 3.5 mg cm^{-2} day^{-1} (Fig. 4) to 0.1 mg cm^{-2} day^{-1} (Fig. 7) when the soil cover thickness increased from 20 to 40 cm. To illustrate the nature of the dependence of volatilization flux on cover thickness, the steady-state form of Eq. 2 can be solved for constant μ_{soil}, with the result:

$$\begin{aligned} J_{\mathrm{g}}(L) &= C_0(\mu_{\mathrm{soil}}D_{\mathrm{soil}})^{1/2}/\sinh(qL) \\ &\approx 2C_0(\mu_{\mathrm{soil}}D_{\mathrm{soil}})^{1/2}\exp(-qL) \end{aligned} \tag{11}$$

where

$$q = (\mu_{\text{soil}}/D_{\text{soil}})^{1/2} \tag{12}$$

Thus, the flux leaving the column decreases exponentially with increasing length, a result similar to that found with a screening model by Jury et al. (1990) for 35 compounds with different chemical and biological properties. In their study, the following equation was derived to calculate the cumulative volatilization loss of a finite initial mass of compound buried beneath a soil cover:

$$V_{\text{c}}^{\text{b}}(\infty)/M_0 = \exp[-L(\mu_{\text{soil}}/D_{\text{soil}})^{1/2}] \tag{13}$$

where $V_{\text{c}}^{\text{b}}(\infty)/M_0$ is the total mass fraction volatilized in infinite time; and L is the soil cover thickness (cm). From this result they calculated the thickness of soil required to reduce volatilization loss to $< 0.7\%$ of the initial mass. When that analysis is applied to our study, the result is 34.5 cm using Eq. 13 and data obtained from expt. *3* for the loam soil used. The values calculated using Eq. 13 for toluene by Jury et al. (1990) in a hypothetical sandy and clayey soil were 80.7 and 15.4 cm, respectively.

5.4. Effect of pre-exposure

The rate of toluene biodegradation was consistently higher in pre-exposed soils than in fresh soils (see Fig. 4 vs. Fig. 7 and Fig. 5 vs. Fig. 6), a result that has been obtained in numerous other studies. Various hypotheses have been proposed to explain this phenomenon, such as growth of the population, induction of enzymes, and selection of new metabolic capabilities produced by genetic changes (Scow et al., 1990). English and Loehr (1991) found that the increase in the removal rate of benzene was due to the increase in the number of microbial colonies with each subsequent addition of benzene. In contrast, Torstensson et al. (1975) observed increased rates of degradation without an increase in the number of organisms able to degrade the test compound in soils exposed to *2,4*-dichlorophenoxyacetic acid (*2,4*-D), and Senior et al. (1976) attributed increased degradation rates to the appearance of a new organism in a mixed microbial population exposed to *2,2*-dichloropropionic acid. Fournier et al. (1981) found no increase in the number of organisms able to metabolize *2,4*-D after exposure to the compound at the concentration of 0.33 mg kg^{-1}, but a significant increase in numbers after exposure at 33 mg kg^{-1}.

Because of the large number of variables potentially involved in enhanced biodegradation, it is difficult to determine the contribution of a change in an individual factor, such as an increase in the growth rate, to the enhancement. This is particularly true in our experimental system where a wide range of toluene concentrations was encountered along the soil column. The microorganisms degrading toluene at various depths did not necessarily follow the same kinetic reaction nor did they even have to be the same species. Therefore, no attempt was made to identify specific mechanisms responsible for the enhancement of toluene degradation in our system.

6. Concluding remarks

With the emergence of in situ bioremediation as an attractive means of waste cleanup, models will be necessary to assist in remediation system design and estimation of cleanup times and efficiency. The parameters required by existing models that describe biodegradation kinetics generally rely on the results of short, simple laboratory experiments reported in the literature. Unfortunately, many kinetic studies have neglected to report the conditions of the soil used in the experiment. The results of this study demonstrate that the exposure history of a soil to the compound of interest is an important variable which significantly affects the experimental results. Therefore, caution should be taken when literature values need to be used in model simulations.

Although this was a laboratory study, our results have implications for bioremediation operations. Pre-treatment of the soil cover with the contaminated chemical to build up an enriched microbial population will shorten the acclimation period prior to the onset of biodegradation at its highest level, and thus will increase the effectiveness of the soil cover in remediation operations. While the practicality of such application to landfill operations may be subject to further discussion due to the large area and large number of chemicals involved in a landfill, it may be a realistic option in treating spills of specific chemicals at smaller scales.

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