Coupled Processes: Diffusive Transport and Biodegradation of Volatile Organic Compounds in Unsaturated Porous Media

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Abstract
Diffusive transport of volatile organic compounds (VOCs) and their degradation by bacteria in unsaturated soils are coupled by poorly understood mass transfer kinetics at the gas/water interface. The capability to predict the fate of VOCs in unsaturated soil is necessary to evaluate the feasibility of natural attenuation as a VOC remediation strategy. The objective of this study was to develop a mechanistically based mathematical model that considered the interdependence of VOC diffusive transport, mass transfer at the gas/water interface, microbial activity, and sorptive interactions in a moist, unsaturated soil. Because the focus of the model was on description of natural attenuation, the advective VOC transport that is induced in engineered remediation processes such as vapor extraction was not considered. The utility of the model was assessed through its ability to describe experimental observations from well-defined experiments in which toluene was used as a representative VOC and diffused through soil columns that contained a toluene degrading bacterium, Pseudomonas putida. The coefficient for gas-liquid mass-transfer, \( K_{La} \), was found to be a key parameter controlling the ability of bacteria to degrade VOCs. This finding indicates that soil size and geometry are likely to be dominant parameters in assessing the possible success of natural attenuation of VOCs in contaminated unsaturated soils.
Introduction
The United States Environmental Protection Agency (USEPA, 1988) has estimated that 0.5 million underground storage tank systems in the United States may be leaking chemicals into soil and groundwater. Volatile organic compounds (VOCs), such as the components of fuels (e.g., benzene and toluene) and solvents (e.g., trichloroethylene and chloroform) are among the most commonly detected subsurface contaminants. VOCs can undergo several transport and transformation processes in unsaturated soil systems. Volatile organic compounds exist in the vapor, liquid, and solid (sorbed) phases under typical conditions in unsaturated soil environments. In the absence of engineered processes that promote advective transport, VOCs in the gaseous phase are transported by molecular diffusion. The magnitude of gaseous diffusion coefficients suggests that diffusive transport of VOCs in the vadose zone should play a major role in their migration and attenuation.

Several factors complicate the understanding of VOC transport in unsaturated soil. The mean free path for molecular diffusion in soils is greater than that in an unobstructed gas phase because of the tortuosity of the pore structure. This change in path length reduces the effective diffusion coefficient. VOCs also dissolve in soil pore water and sorb to soil; therefore diffusion of VOCs is retarded by their interaction with the stationary moist porous medium. Studies of VOC binding in soils have suggested that sorption can involve multiple uptake mechanisms (Chiou and Shoup, 1985; Pennell et al., 1992; Ong and Lion, 1991) including: adsorption and condensation at the gaswater interface, dissolution into stationary pore water, sorption onto soil organic matter, adsorption to mineral surfaces, and diffusion into pores. Additionally, under appropriate conditions, some VOCs are degradable by indigenous soil bacteria. The combination of these transport and reaction mechanisms complicates our ability to predict the fate of VOCs in unsaturated soils.

Accurate prediction of the diffusive transport of VOCs and their degradation is necessary for the assessment of the viability of “natural attenuation” as a treatment strategy for contaminated unsaturated soils. In natural attenuation treatment strategies, no active measures are taken to remove contaminants and natural biological and transport processes are relied upon to degrade, or reduce the concentration of, contaminants. For example, diffusion of VOCs out of soil into the atmosphere results in a loss of contaminant from the soil matrix. Natural attenuation coupled with site monitoring is an appealing treatment strategy because of its very low cost. Natural attenuation strategies are, however, viewed by some as excessively risky because of their passive nature. With an accurate model for the fate of VOCs in unsaturated soil, it would be possible to better predict the performance of natural attenuation strategies and to make rational decisions regarding their utility.

An improved understanding of vapor transport, mass transfer, and degradation is also relevant to biofiltration treatment systems. Although substantial work on the design of biofilters has been performed (for example: Karied et al., 1996; Moller et al., 1996; Smith et al., 1996), creation of mechanistically based models for these systems has not been a priority. In development of a simple biofilter model, Devinny et al. (1993) noted that design of efficient biofiltration systems requires an understanding of the fundamental mechanisms involved.
Several researchers have studied diffusive transport of VOCs in unsaturated porous media (Fan and Scow, 1993; Jin et al., 1994; Peterson et al., 1994). However, prior attempts to model biodegradation coupled with VOC sorption, gas-liquid mass transfer, and diffusion have been unable to describe laboratory observations. The objective of this study was to develop a mechanistically based mathematical model that would consider the interdependence of diffusive VOC transport, microbial activity, mass transfer and sorptive interactions in a moist unsaturated soil. Because the focus of the model was on the description of natural attenuation, the advective VOC transport that is induced in engineered remediation systems for unsaturated soils, such as vapor extraction, was not considered. The utility of the model was assessed through its ability to describe results from well-defined soil column diffusion experiments using toluene as a model VOC. Unlike previous research in this area, the experiments employed a monoculture of a well-characterized toluene-degrading bacterium, *Pseudomonas putida*.

**Materials and Methods**

Soil column experiments in which VOC diffusion, sorption, and degradation all play significant roles were designed and performed to test the validity of the mathematical model. The formulation of the model is described below. Figure 1 shows a schematic of the experimental apparatus. All experiments were performed in a constant temperature environmental chamber at 20 (± 0.2) °C. Analytical grade toluene was used as a model VOC. Toluene was chosen because it is readily degradable under aerobic conditions by many soil bacteria (Jin et al., 1994; Oh et al., 1994) and is a commonly found contaminant in soil (Robinson et al., 1990). An aquifer sand obtained from the Newfield Quarry, Newfield, NY, was used as a porous medium in the column experiments. The sand had an organic carbon content of 1.07 %, a BET surface area of 3.3 m²/g, and a particle size distribution dominated by sand (93 % sand; 6.3 % silt) (Chen et al., 1995). For some experiments, the aquifer sand was sieved and the size fraction <0.212 mm was selected for use to increase the specific surface area of the porous medium and, therefore, increase the importance of mass transfer from the vapor phase. Other physical chemical characteristics of the aquifer material have been reported by Chen et al. (1995). Because indigenous soil bacteria can degrade toluene (Jin et al., 1994), the aquifer sand was sterilized prior to its use in experiments by exposure to 2.5 Mrad γ radiation from the 60Co source in the Ward Reactor Facility at Cornell University.

The bacterium used in these experiments was *Pseudomonas putida*, strain G7, which was obtained by W. Ghiorse from G. Saylor at the University of Tennessee. *Pseudomonas putida* was selected because it has been shown by many researchers to degrade toluene (Duetz et al., 1994; Inoue et al., 1991; Mirpuri et al., 1996; Moller et al., 1996; Oh et al., 1994; Vecht et al., 1988) and to successfully compete with other toluene degraders (Massol-Deya et al., 1997).

An aluminum cylinder 0.30 m in length with an inside diameter of 0.07 m housed the porous medium used in the experiments (see Figure 2). Seven ports, constructed from brass Swagelok® fittings and sealed with Supelco Thermogreen® septa under hollow screw caps, were installed along the length of the column. Toluene concentrations within the soil column were monitored by taking 0.25 mL samples from selected ports using gas tight syringes. Preliminary computer simulations were used to select a sample size and sampling frequency that would not appreciably disrupt diffusive vapor transport during an experiment.
For the purpose of the planned experiments, it was necessary to introduce toluene vapor to the test apparatus in a manner that would permit variation of the source concentration of toluene vapor, avoid inducing VOC advection, and preserve the soil moisture content. A Waters 590 Programmable High Performance Liquid Chromatography pump was used to continuously introduce an aqueous toluene solution at 0.5 mL/min from a source bottle into the influent chamber (50 mL volume) of the test apparatus (see Figures 1 and 2). When the influent chamber of the column had been filled to the desired level, dictated by the height of the drain tube, the toluene solution exited via a drain containing a U-trap to prevent vapor movement. This configuration provided a constant supply of "fresh" toluene and water vapor to the influent chamber where the toluene volatilized from the aqueous phase and entered the soil column. A sampling port covered with a PTFE/silicone septum and aluminum crimp cap allowed the concentration of toluene in the headspace of the influent chamber to be monitored over time.

The effluent chamber of the test apparatus was designed to maintain a low toluene concentration at the end of the soil column, providing a driving force for molecular diffusion. Water saturated air was passed across the top of the soil column to continuously purge toluene from the effluent chamber. Typical sweep gas flow rates of 50 to 100 mL/min provided an adequate concentration gradient for diffusion and yielded easily detectable effluent toluene concentrations. The sweep gas flow rate was quantified with a Precision Scientific Wet Test Meter.

Gas tight Precision Sampling Pressure Lok syringes were used to obtain all VOC samples. Gas samples were analyzed using a Hewlett Packard 5890 series II gas chromatograph equipped with a flame ionization detector and a column packed with 20% SP™-2100 and 0.1% Carbowax-1500 on 100/120 mesh Supelcoport™.

Source solutions of toluene (typically 10 L in volume) were generated by adding liquid toluene to distilled water in glass stoppered flasks (2 L in volume). These flasks were mixed overnight to ensure complete toluene dissolution. The contents of each flask were combined in a 20 L sealed source container where they were mixed for several hours prior to and throughout the course of an experiment.

The headspace method described by Garbarini and Lion (1985) as modified by Peterson et al. (1988) was used to measure the saturated distribution coefficient, $K_d$, for toluene on the sterilized aquifer sand.

*Pseudomonas putida* cultures were prepared in MMS-2 broth (see Table 1) with 2 g/L of pyruvate added as a carbon/energy source. The bacterial cultures were added to the soil when they were in a stationary growth phase so that they would no longer have pyruvate available as a growth substrate and so that the concentration of cells would not change significantly before the experiment began. During cultivation, the cell concentration was monitored periodically by taking OD$_{600}$ readings using a Hewlett Packard 8452A spectrophotometer. When the bacteria reached the stationary growth phase, they were exposed to approximately 10 mg/L of toluene for a 1 h acclimation period. Air was then bubbled through the diluted broth for another hour to purge all residual toluene from the
system. The OD$_{600}$ of the culture was recorded and the broth was diluted with distilled water to yield the cell concentration desired for the soil column experiment. Cell concentrations were calculated using the 0.37 g cells/L-OD$_{600}$ proportionality determined for P. putida G7 by Ahn et al. (1998).

An appropriate volume of the bacterial suspension was added to approximately 1 kg of sterilized sand. The sand was then manually mixed in a shallow container for 5 min to evenly distribute the bacteria. Preliminary experiments in which moisture content was determined independently for ten random samples from sand prepared using this procedure, revealed that effective mixing was achieved via this technique. The aluminum diffusion column was filled with the inoculated sand in small quantities, while being tapped repeatedly to ensure a uniform bulk density.

**Mathematical Model**

Several numerical and analytical models have been developed to describe transport of a volatile gas through unsaturated soil (for example: Gierke et al. 1990, 1992; Jury et al. 1990; Ong et al. 1992, Jin et al. 1994; Peterson et al. 1994). However none of the existing models appeared directly suitable for describing the experimental situations examined in this study because of differences in the boundary conditions imposed, inclusion of processes (such as advective VOC transport) that were not related to this research, assumptions of instantaneous sorption or gas transfer and/or exclusion of necessary processes such as biodegradation. The model used to describe experimental observations obtained in this work is discussed below.

**Influent Concentration of Toluene**

Empirical equations describing the input toluene vapor concentration, $C_o$, as a function of time were derived for each experimental run based upon measured concentrations of toluene in the influent chamber. Initially, the toluene concentration rose rapidly as the gas phase in the influent chamber equilibrated with the aqueous toluene solution. As the toluene solution was pumped from the source bottle, the gaseous to aqueous volume ratio in the sealed source bottle increased, causing the aqueous toluene concentration of the influent stream to decrease over an experimental time frame of about one week. Therefore, after reaching a maximum, the influent toluene concentration in the gas phase declined slightly with time. To maximize agreement with experimental results while minimizing the complexity of the equations involved, two separate empirical equations were used to fit the influent concentration. Typically, the equations used were fifth- or sixth- and first- or second-order polynomials, respectively. In all cases, the resulting influent model curve was compared to the experimental data to confirm that the curve's shape was reasonable. Figure 3 provides a representative example of the influent gas concentration and the numerical fit used to describe the data. The use of fitted equations for the influent gas concentration was to provide input data for the model that best fit the experimental conditions; the large number of significant figures used in the fitted equations was necessary given the high order of the equations.

**Model Derivation**

The computer model was written in Allegro Common Lisp V3.0.2 by Franz, Inc of Berkeley, CA. Euler's method was employed to solve the constitutive equations. The column was
divided into 8 segments and an incremental time-step, \( dt \), of 10 s was used. Preliminary model sensitivity analyses showed that the use of additional segments or shorter time-steps was unnecessary. As an additional check, the model was adapted to evaluate a simple system without biodegradation and the results of the numerical simulation agreed well with those of the corresponding analytical solution (van Genuchten, and Alves, 1982). Toluene concentrations in the gas (\( C_g \)), aqueous (\( C_w \)), and soil (\( S \)) phases were determined for each model segment for each time-step. Initially, all segments were assumed to contain no toluene vapor. The measured initial cell concentration, \( X_0 [M/L^3] \), was set equal to that applied to the soil. Gaseous diffusion was assumed to control the transport of toluene through the column.

The governing equations for the toluene vapor concentration, \( C_g [M/L^3] \), the toluene concentration in stationary pore water, \( C_w [M/L^3] \), and the sorbed concentration of toluene, \( S [M/L^3] \), were:

\[
\begin{align*}
\frac{dC_g}{dt} &= \frac{dC_g}{dt}\text{diffusion} - \frac{dC_g}{dt}\text{gas-liquid transfer} \\
\frac{dC_w}{dt} &= \frac{dC_w}{dt}\text{gas-liquid transfer} - \frac{dC_w}{dt}\text{biodegradation} - \frac{dC_w}{dt}\text{adsorption} \\
\frac{dS}{dt} &= \frac{dC_w}{dt}\text{adsorption}
\end{align*}
\]  

(1) \hspace{1cm} (2) \hspace{1cm} (3)

**Diffusion**

Toluene diffusion through the column was assumed to obey Fick's Second Law. Aqueous diffusion through the column was neglected because of the small magnitude of the aqueous phase diffusion coefficient.

\[
\left(\frac{dC_g}{dt}\right)\text{diffusion} = D_{eff}\left(\frac{d^2C_g}{dx^2}\right)
\]  

(4)

where \( D_{eff} \) is the effective toluene diffusion coefficient (i.e., the free air diffusion coefficient modified for tortuosity) \([L^2/T]\).

**Gas-Liquid Transfer**

Gas-liquid mass transfer was described by the equation:

\[
\left(\frac{dC_w}{dt}\right)\text{gas-liquid transfer} = K_{la}(C_g/H_e - C_w),
\]

(5)

where \( H_e \) is the dimensionless Henry’s Constant [ ] and

\( K_{la} \) is the overall gas-liquid mass transfer coefficient \([T^{-1}]\),

**Sorption**

Sorption of toluene to soil particles was modeled by the equation:

\[
\frac{dS}{dt} = \alpha(C_wK_d - S)
\]

(6)

where \( K_d \) is the water-soil partition coefficient \([L^3/M]\) and

\( \alpha \) is an overall sorption mass-transfer coefficient \([T^{-1}]\) (Abriola et al., 1999).
Biodegradation

Degradation of toluene was assumed to occur in the aqueous phase only. Inhibition kinetics (Andrews, 1968) were assumed because prior investigations of toluene degradation by P. putida supported this assumption (Mirpuri et al., 1996; Oh et al., 1994). The governing equation for biodegradation was therefore:

\[-(dC_w/dt)_{\text{biodegradation}} = \mu_{\text{max}}X C_w/(K_S + C_w + C_w^2/K_I),\]  

(7)

where \(\mu_{\text{max}}\) is the maximum specific utilization rate \([\text{M(substrate)}/\{\text{M(cells)}*\text{T}\}]\),

\(X\) is the biomass concentration \([\text{M(cells)}/\text{L}^3]\),

\(K_S\) is the half-velocity coefficient \([\text{M(substrate)}/\text{L}^3]\), and

\(K_I\) is the substrate inhibition coefficient \([\text{M(substrate)}/\text{L}^3]\).

Cell growth was modeled as:

\[ (dX/dt) = -Y(dC_w/dt)_{\text{biodegradation}} - X*b, \]  

(8)

where \(Y\) is the yield coefficient \([\text{M(cells)}/\text{M(substrate)}]\) and

\(b\) is the cell death rate \([\text{T}^{-1}]\).

Dimensionless Equations

To generalize the model, the constitutive equations were rendered dimensionless. The following dimensionless variables were defined:

\[ C_g' = C_g/C_0, \]  

(9)

\[ C_w' = C_w/C_0, \]  

(10)

\[ X' = X/X_0, \]  

(11)

\[ Z' = z/L, \text{ and} \]  

(12)

\[ t' = t/t_c, \]  

(13)

where \(L\) is the length of the column \([\text{L}]\),

\(t_c\) is the characteristic time for diffusion (see below) \([\text{T}]\),

\(Z'\) is the dimensionless form of \(z\), and

all other starred terms are dimensionless forms of their non-starred counterpart.

By substituting the dimensionless variables in equations (5) through (8), the following dimensionless equations result:

\[ C_0/t_c*(dC_g'/dt)_{\text{diffusion}} = C_0/L^2*D_{\text{eff}}*[d^2C_g'//(dz')^2] \]  

(14)

\[ C_0/t_c*(dC_w'/dt)_{\text{mass transfer}} = C_0*K_La*(C_g'/H_c - C_w'), \]  

(15)

\[ C_0/t_c*(dS'/dt)_{\text{adsorption}} = C_0*\alpha*(C_w'*K_d - S) \]  

(16)

\[ C_0/t_c*(dC_w'/dt)_{\text{biodegradation}} = C_0*X_0*\mu_{\text{max}}*X'*C_w'/[K_S + C_0*C_w' + (C_0*C_w')^2/K_I], \]  

(17)

\[ X_0/t_c*(dX'/dt') = Y*(dC_w'/dt)_{\text{biodegradation}} - X*X_0*b, \]  

(18)
Based upon equations (14) through (17), the dimensionless forms of equations (1), (2), and (18) are:

\[
\frac{dC_g^*}{dt^*} = \left( \frac{d^2C_g^*}{dz^*} - t_e \cdot K_{La} \cdot (C_g^*/H_c - C_w^*) \right) V_g/V_w
\]

\[
\frac{dC_w^*}{dt^*} = t_e \cdot K_{La} \cdot (C_g^*/H_c - C_w^*) - t_e \cdot \alpha^* (C_w^* K_d - S) \cdot \rho_w/MC
\]

\[
\quad - t_e \cdot X_0 \cdot \mu_{max} \cdot X^* C_w/[K_w + C_0 \cdot C_w^* + (C_0 \cdot C_w^*)^2/K_i]
\]

\[
\frac{dX^*}{dt^*} = C_0 \cdot t_e \cdot Y^* \cdot \mu_{max} \cdot X^* C_w/[K_w + C_0 \cdot C_w^* + (C_0 \cdot C_w^*)^2/K_i] - t_e \cdot X^* b
\]

where $V_g$ is the volume of the gaseous phase in a segment [L$^3$],

$V_w$ is the volume of the liquid phase in a segment [L$^3$],

MC is the moisture content [M(water)/M(water and soil)],

$\rho_w$ is the density of water (assumed equal to 1.00 g/mL), and

the characteristic time is $t_e = L^2/D_{eff} [T]$ (chosen to eliminate the coefficient to the second-order term in equation 14).

The terms $V_g/V_w$ and $\rho_w/MC$ convert $C_w$ units to $C_g$ units and $S$ units to $C_w$ units, respectively. Equation (16) is the dimensionless form of equation (4). Equations (16), (19), (20), and (21) are the constitutive equations employed by the computer model.

**Model Parameters**

The computer model relies upon knowledge of several parameters. Some of these parameters, such as $L$ and $A$, were determined by the apparatus design and were constant for all experiments, others (such as $M.C.$, and $Q_0$) were measured separately for each experimental run. The remaining parameters were estimated either from literature values or determined by experimental analyses. Table 2 lists all model parameters. The parameters listed as “determined” were experimentally derived as part of this study. “Estimated” variable values were chosen from values reported by other researchers and in some cases were selected from a large range of reported literature values.

**Results and Analysis**

The effective diffusion coefficient was estimated by assuming steady state and negligible biodegradation at long run times and employing the following two equations for mass flux, $J$:

\[
J = D_{eff} \cdot [(C_0 - C)/L]
\]

\[
J = Q_e \cdot C/A
\]

where $C$ is the effluent gaseous toluene concentration [M/L$^3$].

Equating equations (22) and (23) yields the following equation for $D_{eff}$:

\[
D_{eff} = Q_e \cdot C \cdot L/[A \cdot (C_0 - C)]
\]

Analysis of model data showed that $K_{La}$ was very low in experiments with inoculated soil and non-sieved sand. The sample port gaseous toluene concentrations for one representative experiment are shown in Figure 4. It was impossible to model this data, and the data from two similar experiments, while using high values of $K_{La}$ unless the experimentally determined parameter $D_{eff}$ was altered.
The model simulations shown in Figure 4 employ the measured $D_{\text{eff}}$ of 0.0180 cm$^2$/s and the $K_{l,a}$ used for the illustrative model fit was 2.24x$10^{-5}$ s$^{-1}$. The impacts of biodegradation and sorption are masked at low $K_{l,a}$. Consequently, the values of the bacterial kinetic parameters, $\alpha$, and $K_{d}$ had a negligible influence on the simulation shown in Figure 4 and the assumption of negligible biodegradation needed to determine $D_{\text{eff}}$ was satisfied.

Figure 5 shows the model's prediction of various toluene concentrations and transfer rates at column sample port 4 (i.e., column midpoint) for the experiment shown in Figure 4. Note that the gaseous toluene concentration is in units of mg gaseous toluene/L while all other variables, except transfer rates, are in aqueous concentration units. The variation in gaseous toluene concentration is small despite the interesting dynamics in the simulated magnitude of biodegradation and gas-liquid mass transfer rates that occur at approximately 1200 min.

Figure 5 demonstrates that the rate limiting process for this experiment was mass transfer from the gaseous phase to the aqueous phase. The calculated gaseous and aqueous toluene concentrations clearly do not obey Henry's Law equilibrium [the dimensionless Henry's Constant for toluene at 20 °C is 0.268 (Metcalf & Eddy, 1991)] and the lines for the biodegradation rate and the gas-liquid mass transfer rate are approximately equal after about 2000 min. This simulation reveals that the amount of toluene entering the aqueous phase from the gaseous phase is equal to the amount of aqueous toluene degraded. Because the overall VOC mass transfer rate was low, bacterial degradation of toluene did not have a significant influence on the observed results.

To verify that $K_{l,a}$ was a rate-limiting kinetic factor, $K_{l,a}$ was increased by sieving the soil using a No. 70 sieve (thereby removing all particles greater than 0.212 mm in diameter). An experiment with the sieved soil very clearly exhibited evidence of microbial activity (see Figure 6). The somewhat erratic decline in toluene concentration with time in this experiment suggested possible experimental error. However, the results are remarkably similar to the findings of Jin et al. (1994) who also observed fluctuations in gas concentration. While the experiment with sieved sand employed higher moisture content than the experiment with non-sieved sand, it should be noted that an experiment with a non-sieved sand at a moisture content of 0.082, yielded results similar to those shown in figure 4.

Figure 7 shows the model fit to the experimental data for the sieved sand at one sample port. Note that the $K_{l,a}$ value used in the model was chosen to achieve a toluene breakthrough curve similar to that observed. The effective diffusion coefficient in this experiment could not be estimated with equation (25) because that relationship neglects the possible presence of any toluene sinks present in the soil column. Additionally, equations (23) and (25) assume a linear concentration gradient throughout the column and this assumption in not valid when significant microbial activity occurs. For this reason, the $D_{\text{eff}}$ value measured for the unsieved experiment shown in Figure 4 was employed for the model calculations. It is acknowledged that the actual $D_{\text{eff}}$ could possibly be lower because of the high moisture content of the sieved sand and the smaller grain size; however reasonable changes in $D_{\text{eff}}$ do not have a significant impact on the qualitative trend of the model simulations.
Research by Mirpuri et al. (1996) and Oh et al. (1994) both suggest K_I values of roughly 43 mg toluene/L for P. putida. Model simulation of the data from the experiment with sieved aquifer material, particularly the almost simultaneous decrease in gaseous toluene concentration at ports 3 and 5, could not be achieved with this value. Consideration a higher value for K_I, which may be justified given differences in bacterial strains and growth medium, allowed the observed behavior to be modeled without using an unrealistically high D_{eff}. Despite the changes in K_I, the model simulation was unable to duplicate the oscillations in toluene vapor content that were observed; however, the general trend of the model simulation closely matches the observed vapor toluene concentration profile.

The model parameters used for the simulation of the experiments with sieved and non-sieved aquifer material are shown in Table 3. Note that it was possible to predict the trends in each experiment while keeping sorption and microbial kinetic parameters the same. The success of the model for these two cases suggests that K_{L,a} was, in fact, the limiting kinetic factor in the experiment with the non-sieved material.

Conclusions
The erratic degradation of toluene by soil bacteria observed by Jin et al. (1994) was duplicated in this research. Jin et al. attributed the general decline in toluene concentration to either bacterial growth or improved microbial activity caused by prolonged exposure to the toluene. Because the model described here was able to reproduce the general trend in the gaseous toluene concentration without considering changes in microbial activity, we believe that bacterial growth is most likely to be the causative factor for the decrease in toluene concentration with time.

Jin et al. also provided some possible explanations for the erratic behavior in toluene concentration that were similarly observed in this study. They conjectured that the oscillations “could have been caused by the interactions of many processes such as overshooting of microbial growth, rate-limited diffusion, and possible competition between different microbial species.” In this research a pure bacterial monoculture was used, ruling out bacterial competition as an explanation for fluctuations in the VOC concentration. The other two mechanisms suggested by Jin et al. are taken into account by the model described here, but the model simulations cannot produce the observed toluene fluctuations. Furthermore, the frequency of the oscillations was on the order of 24 h for the Jin et al. experiment and as long as 12 h for this study. With a doubling time around 2 h for P. putida and a vapor breakthrough time of 2 h, it seems unlikely that either microbial growth or diffusion can responsible for the observed fluctuations. The experimental conditions and apparatus used by Jin et al. (1994) differ from that of this research in many significant respects. Thus a common analytical or procedural error is unlikely to explain the similar observations obtained in both studies.

It was hypothesized that the oscillations in VOC concentration could have been caused by the formation of a toxic intermediate that inhibited the bacterial population. Several model modifications were tested in an attempt to predict the effect of a hypothetical byproduct. These model modifications included both zero and first order byproduct decay rates, first order impacts of a byproduct on the bacterial death rate, b, and/or maximum growth rate, μ_{max}, both with and without threshold byproduct levels, and time-delayed (up to 10 min)
effects of the inhibitory byproduct. None of the conditions tested produced simulations that had oscillations in the toluene concentration and the explanation for these observations awaits further research.

The model simulations illustrate the importance of $K_{La}$ on the steady state effluent VOC concentration when bacteria are present. The rate of biodegradation is ultimately limited by the rate at which the VOC can enter the aqueous phase through mass transfer from the gaseous phase. Bacterial growth parameters, such as the specific utilization rate and the yield coefficient, are irrelevant at steady state. With a lower $\mu_{max}$, for example, the steady state cell concentration would be higher, resulting in the same VOC degradation rate.

The success of natural attenuation as a remediation strategy appears to be dictated by the relative magnitudes of $D_{eff}$ and $K_{La}$. This fact becomes evident when the nature of VOC contaminant transport is considered. The effective diffusion coefficient controls the rate at which the VOC leaves the contaminant site. If this value is high relative to $K_{La}$, then the contaminant is able to escape the soil matrix without being appreciably degraded. At increasingly higher $K_{La}$ values, the VOC dissolves into the pore water where it is susceptible to bacterial degradation, resulting in reduced contaminant release to the atmosphere. From a practical perspective, high values for moisture content, soil fineness, soil roughness, and VOC affinity for water, and a low value VOC diffusion coefficient are desirable for effective degradation. Note however that, if the VOC affinity for water is too high (i.e., low Henry's law constant), then the VOC will not enter the gaseous phase readily. In this case, or when the VOC diffusion coefficient is low, bacterial degradation of the contaminant will be restricted to the soil region near the source.

To successfully employ natural attenuation as a remediation strategy, at least two additional factors must be considered. An appropriate bacterial species (i.e., one that can degrade the VOC in question at the concentrations of VOC that will be available) must be present in the soil or be available to add to the soil matrix. This requirement leads directly to the next important factor: soil moisture conditions and nutrient levels must be capable of supporting the necessary bacterial population. Although bacterial kinetics are unimportant for the steady state VOC degradation rate they do dictate the microbial concentration required to produce this degradation rate. Nutrients, including soil moisture itself, must be sufficiently available to support the necessary population.

Through modeling techniques, such as those employed in this study, a feasibility analysis could be performed for sites that are potential candidates for natural attenuation. Experimental estimation of $K_{La}$ and $D_{eff}$ would be needed and when coupled with rough estimates of bacterial kinetic parameters, could be used to assess whether natural attenuation is a treatment alternative worthy of additional consideration. For those sites at which natural attenuation appears promising, more thorough experimentation could then be performed to determine model parameters and improve its predictive utility.

Acknowledgements

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References


TABLE 1. Composition of the minimal mineral salts (MMS) liquid medium for cell growth

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (balance distilled, deionized water)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(mg/L)</td>
</tr>
<tr>
<td>Pyruvate</td>
<td>240</td>
</tr>
<tr>
<td>CaCl₂·2H₂O</td>
<td>30</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
<td>35</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>120</td>
</tr>
<tr>
<td>KNO₃</td>
<td>15</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.84</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>0.70</td>
</tr>
<tr>
<td>Vitamin B12</td>
<td>0.002</td>
</tr>
<tr>
<td>FeSO₄</td>
<td>0.015</td>
</tr>
</tbody>
</table>

Initial pH = 6.0.
Ionic strength was adjusted to 0.05 M w/ NaNO₃.
### Table 2: Model parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Units</th>
<th>Type</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Cross-sectional area of soil column</td>
<td>cm²</td>
<td>Apparatus design</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td><em>P. putida</em> death rate</td>
<td>d⁻¹</td>
<td>Estimated</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>C₀</td>
<td>Maximum influent toluene concentration</td>
<td>mg/L</td>
<td>Determined</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dₑff</td>
<td>Effective toluene diffusion coefficient</td>
<td>cm²/s</td>
<td>Determined</td>
<td>Varied</td>
<td></td>
</tr>
<tr>
<td>Hₑ</td>
<td>Dimensionless Henry's Constant</td>
<td></td>
<td>Estimated</td>
<td>0.268</td>
<td>Metcalf &amp; Eddy (1991)</td>
</tr>
<tr>
<td>Kₑd</td>
<td>Soil-water partition coefficient</td>
<td>mL/g</td>
<td>Determined</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>Kₑa</td>
<td>Overall mass transfer coefficient</td>
<td>d⁻¹</td>
<td>Estimated</td>
<td>50</td>
<td>Abriola <em>et al.</em> (1999)</td>
</tr>
<tr>
<td>Kₐ</td>
<td>Inhibition coefficient</td>
<td>mg/L</td>
<td>Estimated</td>
<td>43</td>
<td>Mirpuri <em>et al.</em> (1996), Oh <em>et al.</em> (1994)</td>
</tr>
<tr>
<td>Kₛ</td>
<td>Half velocity coefficient</td>
<td>mg/L</td>
<td>Estimated</td>
<td>15</td>
<td>Mirpuri <em>et al.</em> (1996)</td>
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<tr>
<td>L</td>
<td>Length of soil column</td>
<td>cm</td>
<td>Apparatus design</td>
<td>30.5</td>
<td></td>
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<tr>
<td>MC</td>
<td>Moisture content</td>
<td></td>
<td>Measured</td>
<td>varied</td>
<td></td>
</tr>
<tr>
<td>Qₛ</td>
<td>Sweep gas flow rate</td>
<td>mL/s</td>
<td>Measured</td>
<td>varied</td>
<td></td>
</tr>
<tr>
<td>X₀</td>
<td>Initial <em>P. putida</em> concentration</td>
<td>mg/L</td>
<td>Measured</td>
<td>varied</td>
<td></td>
</tr>
<tr>
<td>α</td>
<td>Overall sorption mass transfer coefficient</td>
<td>d⁻¹</td>
<td>Estimated</td>
<td>5</td>
<td>Abriola <em>et al.</em> (1999)</td>
</tr>
<tr>
<td>ρₑ</td>
<td>Density of water</td>
<td>g/mL</td>
<td>Estimated</td>
<td>0.998</td>
<td>Metcalf &amp; Eddy (1991)</td>
</tr>
<tr>
<td>μₘₙₓ</td>
<td>Maximum specific utilization rate for <em>P. putida</em></td>
<td>mg tol/ (mg*d)</td>
<td>Estimated</td>
<td>17.28</td>
<td>Oh <em>et al.</em> (1994)</td>
</tr>
</tbody>
</table>

### Table 3: Model parameters used to simulate experimental results for non-sieved and sieved aquifer sand.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>X₀ (mg/L)</th>
<th>Dₑff (cm²/s)</th>
<th>MC</th>
<th>Qₛ (mL/s)</th>
<th>C₀ (mg/L)</th>
<th>Kₑd (mL/g)</th>
<th>α⁻¹</th>
<th>Kₑa s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-sieved</td>
<td>2.22E-4</td>
<td>0.0180</td>
<td>0.045</td>
<td>1.42</td>
<td>12.0</td>
<td>2.1E-3</td>
<td>3.1E-6</td>
<td>2.24E-5</td>
</tr>
<tr>
<td>Sieved</td>
<td>2.76E-3</td>
<td>0.0180</td>
<td>0.080</td>
<td>1.25</td>
<td>65.0</td>
<td>2.1E-3</td>
<td>3.1E-6</td>
<td>4.92E-4</td>
</tr>
</tbody>
</table>
Figure Captions

Figure 1. Schematic of experimental apparatus.

Figure 2. Schematic of diffusion test cell.

Figure 3. Typical source toluene concentration profile. Equations shown are those used to fit the data for purposes of model input.

Figure 4. Toluene concentration at sample ports 2, 4, and 6 for a diffusion experiment with non-sieved aquifer sand. Symbols show experimental data and lines shown are for model simulations.

Figure 5. Model simulations of the conditions at the column midpoint for the experiment with non-sieved aquifer sand.

Figure 6. Observed toluene concentrations for source, Port 5, and Port 3 for the experiment with sieved aquifer sand.

Figure 7. Toluene Concentration at Port 3 for the experiment with the sieved aquifer sand. Symbols show experimental data and the line shown is for the model simulations.
y = -9.16861715370315E-04x + 1.18017134812413E+01

y = 5.54320567619293E-12x^5 - 7.89530999842250E-09x^4 + 4.19366028235266E-06x^3 - 1.05010720928655E-03x^2 + 1.39708754765735E-01x + 9.81093808247806E-02