

Benzene vapor transport in unsaturated soil: Adequacy of the diffusion equation

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(Received October 7, 1992; accepted in revised form February 15, 1993)

Abstract

Experimental data for unsteady state benzene vapor transport in large (10.5 cm × 100 cm) columns packed with dry and wet soil were used to evaluate the adequacy of the diffusion equation. It was shown that the diffusion equation and local equilibrium, accounting for water phase partitioning and linear sorption, adequately described vapor transport in dry soil. In wet soil, however, possible benzene biodegradation resulted in deviation of the diffusion equation from the experimental data. At steady-state, the dimensionless vapor concentration versus distance profile for the dry soil was linear, as opposed to the same profile in the wet soil column. The best fit retardation factor of benzene vapor for wet soil ($R=12$) was lower than that for dry soil ($R=46$), because of a reduction in vapor sorption capacity, due to competition with water molecules. A vapor phase sorption coefficient, $K_d=5.05 \text{ cm}^3/\text{g}$, was computed for the dry soil and $K_d=0$ for the wet soil.

Introduction

Volatile Organic Chemicals (VOCs) can be introduced in the subsurface environment as Non-Aqueous Phase Liquids (NAPLs) in a variety of ways. These include Leaking Underground Storage Tanks (LUSTs) and pipelines, accidental spills, land disposal sites, and industrial waste impoundments. Volatilization of NAPLs may result in significant mass transport of organic vapors away from the NAPL source. Since vapor migration is important with respect to very practical problems, such as site remediation by soil venting, leak detection from LUSTs, and contamination of clean groundwater, it is essential to understand the processes affecting vapor transport.

In most modeling studies, the simulation of vapor diffusive fluxes was quantified by Fick's laws of diffusion [1–5]. With a few exceptions [6], most models assumed local equilibrium for mathematical simplicity. Thus, mass transfer

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processes between different phases were described by partition coefficients, such as Henry's constant and linear solid–liquid and solid–gas sorption coefficients [3, 4]. Most of the models developed for vapor phase diffusion lack laboratory or field studies to verify their validity. Some experimental studies exist, which were conducted in 3 cm × 2 cm × 10 cm volatilization cells [7, 8], or 1.5 cm × 7.5 cm volatilization columns [9].

The objectives of this work were to assess the adequacy of the diffusion equation in describing non-steady-state experimental diffusion data for benzene vapor in unsaturated soil. The diffusion equation accounting for water phase partitioning and linear sorption isotherm was fitted to experimental concentration profiles of benzene vapor for dry and wet soil. Best fit retardation factors were used to determine linear vapor phase sorption coefficients, which were then used to assess the effect of moisture on gas phase sorption.

Benzene was used because of its significant water solubility (1780 mg/L), volatility (vapor pressure of 10.1 kPa), high toxicity, and abundance in subsurface contaminated sites, as a common component of gasoline and other petroleum products. Diffusion experiments were conducted using large columns (10.5 cm × 100 cm) packed with dry and wet soil. Experimental concentration profiles were established by analyzing vapor samples at different times and distances from the vapor source. There are several advantages in using large size diffusion columns. For example, a larger and more representative soil sample can be used. It is easier and more accurate to observe vapor concentration profiles along the column length in larger than in smaller columns. Compared to small breakthrough columns with advective transport, the large diffusion columns provide longer residence times and are less likely to be subject to mass transfer limitations or practical flow problems in high clay, low permeability soils. To our knowledge, non-steady-state experimental diffusion data in large scale columns packed with soil other than sand have not been published in the peer-reviewed literature.

Materials and methods

Soil characterization

Soil used in this research was from a wooded depression, south of Waycross, Georgia. The soil was collected from a depth of 20–50 cm and was stored in black plastic bags at 7 °C. Representative aliquots were employed for determination of soil composition, particle-size distribution, moisture content, particle density, surface area, and organic carbon content. From the above results water-filled porosity, air-filled porosity, and total porosity were calculated.

The soil was taken out of the 7 °C room and spread on large plastic sheets to remove part of the moisture under room temperature. Then, it was passed through a 0.85 mm sieve (ASTM Sieve Number 20) to remove large debris. For wet soil column experiments, the soil was completely mixed and partially

air-dried at room temperature, whereas for dry soil column experiments the soil was completely mixed and oven-dried for 12 hours at 80°C.

Particle size distribution was obtained by passing the soil through a series of sieves [10]. Moisture content was determined according to Gardner [11], by heating a soil sample of known size at 103°C until constant weight. The particle density of each soil used was determined according to Blake and Hartge [12], by measuring the mass and the volume of the soil sample. The surface area was determined by using a single point BET method using N₂ and was an external surface area instead of total surface area [13].

Organic carbon of the soil was determined from the difference of total carbon and inorganic carbon content using the Total Carbon Apparatus (Model 5020, Coulometrics, Inc., Golden, CO). The carbon dioxide produced from combustion of a soil sample in an oxygen atmosphere was determined using a micro-coulometer and was converted in percentage total carbon. Inorganic carbon was determined by acidification of the sample in a heated vessel, purging, trapping, and measuring carbon dioxide of inorganic origin.

After soil columns were packed, bulk density and porosities were determined using the following equations:

$$\rho_b = W/V \quad (1)$$

$$\varepsilon_T = 1 - \rho_b/\rho_p \quad (2)$$

$$\varepsilon_w = M\rho_b/\rho_w \quad (3)$$

$$\varepsilon_a = \varepsilon_T - \varepsilon_w \quad (4)$$

where ρ_b is the bulk density on dry weight basis (g/cm³), W is the mass of oven-dried soil packed in column (g), V is the total volume occupied by soil (cm³), ε_T is the total porosity, ρ_p is the particle density (g/cm³), ε_w is the water-filled porosity, M is the moisture content (mass of water/mass of oven-dried soil), ρ_w is the water density (g/cm³), and ε_a is the air-filled porosity.

Column experiments

Glass columns 10.5 cm i.d. and 100 cm long were used for the soil column experiments. Each column was equipped with six sampling ports located along the column axis at distances 0, 8.6, 18.4, 38.6, 58.4, and 78.3 cm, respectively, from the inlet end, as shown in Fig. 1. Each sampling port included a cylindrical glass septum holder, 5 mm i.d. and 10 mm high. A teflon-lined septum (HGC-138, Analabs, Inc., New Haven, CT) was placed into each septum holder. Then, a perforated 10 cm long 18 gauge stainless steel needle was inserted through the septum of each sampling port. A cleaning wire was kept inside the needle to prevent entrance of soil during the insertion step. The Luer hub of each needle was plugged with a two-way Mininert Teflon Valve (Alltech Associates, Inc., Deerfield, IL) which, when open, allowed the insertion of a gas-tight syringe for vapor sampling. Two layers of a 80 mesh stainless steel screen supported on a 1.2 cm thick and 1 cm wide circular aluminum ring were

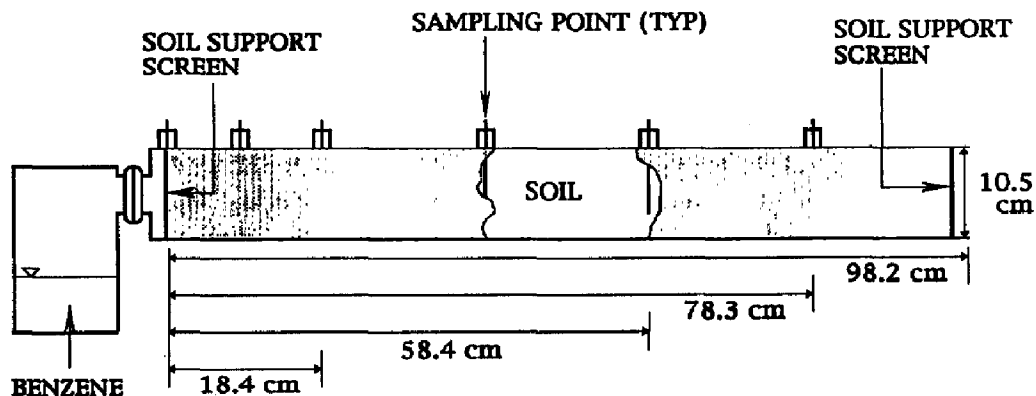


Fig. 1. Experimental column setup for benzene vapor transport experiments.

used on each end of the glass column to support the soil. The inlets of all soil columns were connected to a reservoir containing approximately 200 mL of benzene. Prior to starting each vapor experiment, the benzene reservoir was connected to a different but similar soil column to allow the establishment of steady-state vapor concentration, i.e., constant source strength at sampling port #1. Then, the reservoir was connected to the actual soil column and measurement of time was started. All experiments were conducted in a 20 °C constant temperature room. The column outlet was open and the soil was exposed in the atmosphere of the constant temperature room.

Each column was packed by adding soil in portions of 100 cm³ at the surface of previously added soil, using a scoop attached to the end of a 100 cm aluminum rod. After each soil addition, the column was compacted by hand in a uniform fashion using a 3 cm diameter and 120 cm long wooden rod. This procedure minimized the stratification of soil in the column. The experimental conditions and particle size distribution of the soil used in both columns are summarized in Tables 1 and 2. A water-filled micromanometer was used in an attempt to measure pressure gradients within the soil column. Such gradients could result from sample withdrawing or barometric pressure fluctuations at the open end of the column. No measurable pressure gradients were observed, however.

Vapor sample analysis

Benzene vapor samples, 0.1 mL in volume were taken with a gastight syringe (Hamilton, Reno, NV) and periodically analyzed by gas chromatography (GC). Such sample size would prevent overloading of the GC detector and account for total gas volume withdrawn by all samples during the course of the experiment, of less than 1% of the total void space of each soil column.

All benzene vapor samples taken from column experiments were analyzed by GC (Model 5710A, Hewlett Packard) equipped with flame ionization detector and an integrator (Model 3380A, Hewlett Packard). A DB-1 capillary column 30 m long and 0.55 mm in diameter (J and W Scientific, Inc., Folsom, CA) was

TABLE 1

Experimental conditions for the soil columns

Condition	Benzene	
	Dry soil	Wet soil
Volume of NAPL, mL	200	200
Temperature, °C	20	20
Column diameter, cm	10.5	10.4
Column length, cm	97.1	97.1
Mass of soil ^a , g	12,649	12,629
Moisture content ^b , %	0.067 (0.005) ^c	8.86 (0.03)
Organic carbon ^b , %	1.54 (0.022)	1.54 (0.022)
Bulk density ^b , g/cm ³	1.50	1.40
Particle density ^b , g/cm ³	2.51 (0.003)	2.44 (0.04)
Total porosity	0.400	0.428
Air-filled porosity	0.399	0.304
Water-filled porosity	0.001	0.124
External surface area ^b , m ² /g	1.45	1.45

^a Wet mass basis,

^b Dry mass basis,

^c Numbers in parentheses represent standard deviation.

TABLE 2

Particle size distribution of soil used in column experiments

Particle size (mm)	% Mass	
	Dry soil	Wet soil
> 0.85	1.1	1.1
0.85-0.425	20.0	19.0
0.425-0.25	22.2	20.9
0.25-0.15	19.4	19.1
0.15-0.106	17.6	18.3
0.106-0.075	12.4	13.1
< 0.075	7.3	8.5

used. The GC was operated under an isothermal temperature of 100 °C. Injection port and detector temperatures were 150 and 200 °C, respectively. In all experiments, vapor samples were injected with a 250- μ L gastight syringe (Hamilton, Reno, NV) equipped with a two-way valve and side-port needle

(Hamilton, Reno, NV). Instrument response versus concentration curves were generated each day vapor samples were to be analyzed.

Transport model for the unsaturated soil columns

Diffusion equation

The one-dimensional conservation of mass equation with no chemical or biological reactions for benzene in isothermal, isotropic, and homogeneous unsaturated soil, without gas and liquid phase advection, takes the form of the well known diffusion eq. [3]:

$$\frac{\partial G}{\partial t} = D \frac{\partial^2 G}{\partial x^2} \quad (5)$$

where G is the benzene vapor concentration in air (g/cm^3), t is the time (s), x is the distance (cm), and D is the overall diffusion coefficient for benzene (cm^2/s).

Using the local equilibrium assumption to describe vapor distribution between the water, air, and soil phases, D can be calculated from the following equations [3]:

$$D = \frac{D_w/K_H + D_a}{\varepsilon_a R} \quad (6)$$

$$D_w = D_w^b \varepsilon_w \tau_w \quad (7)$$

$$D_a = D_a^b \varepsilon_a \tau_a \quad (8)$$

$$\tau_w = \frac{\varepsilon_w^{7/3}}{\varepsilon_T^2} \quad (9)$$

$$\tau_a = \frac{\varepsilon_a^{7/3}}{\varepsilon_T^2} \quad (10)$$

$$K_H = G/C \quad (11)$$

$$R = 1 + \left(\frac{1}{\varepsilon_a K_H} \right) (\varepsilon_w + K_{\text{obs}} \rho_b K_H) \quad (12)$$

where D_w , D_a are the effective diffusion coefficients of benzene in water and air, respectively, in the porous medium (cm^2/s); D_w^b , D_a^b are the molecular diffusion coefficients of benzene in bulk water and bulk air, respectively (cm^2/s); K_H is the air-water partition coefficient (Henry's constant); τ_w , τ_a are the water phase and air phase tortuosity, respectively; C is the benzene concentration dissolved in water (g/cm^3); K_{obs} is the overall linear sorption coefficient, accounting for both liquid and vapor phase sorption (cm^3/g); and R is the retardation factor.

In eq. (12), R can be interpreted as a retardation factor for the vapor plume taking into account both liquid and vapor phase sorption. The importance of

vapor phase sorption was discussed by Shoemaker et al. [4]. In order to include vapor phase sorption, we propose eq. (13), assuming a linear sorption isotherm:

$$S = K_{\text{obs}}G = K'_dG + \frac{K_d}{K_H}G \quad (13)$$

with

$$K_{\text{obs}} = K'_d + \frac{K_d}{K_H} \quad (14)$$

where S denotes the benzene concentration sorbed by soil (g/g), K'_d the linear sorption coefficient for vapor phase sorption, strong function of ε_w (cm^3/g), and K_d the linear soil–water partition or sorption coefficient (cm^3/g).

Depending on the soil moisture conditions, the values of K_d and K'_d may be determined as follows: At high moisture contents, ranging from soil surface coverage with more than five layers of water molecules to water retention capacity of the soil, $K'_d = 0$ and $K_{\text{obs}} = K_d/K_H$ [14, 15]. At intermediate moisture contents, corresponding to soil surface coverage with one to five layers of water molecules, K'_d decreases with increasing ε_w . K'_d corresponds to vapor sorption onto surface bound water, limited vapor dissolution into sorbed water [14, 15], and direct vapor sorption onto mineral surfaces, assuming the existence of such surfaces not covered by water molecules, due to soil heterogeneity. For this moisture region, we assumed that K_d is not a function of ε_w , although, in reality, K_d is expected to decrease, once ε_w drops below a critical value, ε_{wc} [16]. At extremely low ε_w , corresponding to soil surface coverage with less than one water layer, it is assumed that $K_d = 0$ and $K_{\text{obs}} = K'_d$, which is a strong function of ε_w .

The constants K_{obs} , K_d , and K'_d must be measured experimentally — K_d can also be computed from empirical correlations. Equation (15) (see Curtis et al. [17] and references therein) was used whenever an independent estimate for the liquid phase sorption coefficient was necessary:

$$K_d = K_{oc} f_{oc} \quad (15)$$

where K_{oc} is the organic carbon partition coefficient (cm^3/g), and f_{oc} the organic carbon fraction of soil.

Henry's constant, K_H , was calculated from eq. (11), using benzene solubility of 1780 mg/L [18] and saturated vapor concentration above liquid benzene of 325 mg/L calculated from ideal gas law and vapor pressure of 10.1 kPa [19]. The calculated value $K_H = 0.183$ is in close agreement with that measured by Mackay et al. [20], after temperature correction and unit conversion. The parameters of ε_T , ε_w , and ε_a were determined from eqs. (2), (3), and (4), respectively. Air and water phase tortuosities, τ_a and τ_w , were determined from eqs. (9) and (10), the Millington–Quirk model [21]. The value for D_a^b was taken as $9.32 \times 10^{-2} \text{ cm}^2/\text{s}$ [22]. This value is in close agreement with that determined by the Wilke–Lee equation [23], $D_a^b = 9.33 \times 10^{-2} \text{ cm}^2/\text{s}$.

TABLE 3

Input parameters to diffusion model for benzene

Parameter	Value	Equation or reference
G	325 mg/L	Weast [19]
C	1780 mg/L	Mackay and Shiu [18]
V_m	96 cm ³ /mol	Lyman et al. [23]
ϕ_w	2.6	Lyman et al. [23]
K_H	0.183	Eq. (11)
τ_w	6.25 × 10 ⁻⁷ (dry soil)	Eq. (9)
τ_w	0.0419 (wet soil)	Eq. (9)
τ_a	0.733 (dry soil)	Eq. (10)
τ_a	0.340 (wet soil)	Eq. (10)
D_w^b	9.59 × 10 ⁻⁶ cm ² /s	Eq. (16)
D_a^b	9.32 × 10 ⁻² cm ² /s	Lugg [22]
D_w	4.80 × 10 ⁻⁹ cm ² /s (dry soil)	Eq. (7)
D_w	5.93 × 10 ⁻⁷ cm ² /s (wet soil)	Eq. (7)
D_a	2.73 × 10 ⁻² cm ² /s (dry soil)	Eq. (8)
D_a	9.63 × 10 ⁻³ cm ² /s (wet soil)	Eq. (8)

Bulk diffusivity in water was calculated from the Wilke-Chang equation [23] (Table 3):

$$D_w^b = \frac{7.4 \times 10^{-8} (\phi_w M_w)^{0.5} T}{\mu V_m^{0.6}} \quad (16)$$

where ϕ_w is the solution association constant (2.6 was used for aqueous solution), M_w is the molecular weight of water (g/mol), T is the temperature (K), μ is the solution viscosity (cP, or mPa s), and V_m is the benzene molal volume at normal boiling point (cm³/mol).

Solution of the diffusion equation

The initial and boundary conditions for the column system (Fig. 1) are:

$$\text{I.C.} \quad G=0, t=0, \quad x>0 \quad (17)$$

$$\text{B.C.s} \quad G=G_0, t>0, \quad x=0 \quad (18)$$

$$G=0, t>0, \quad x=L \quad (19)$$

where G_0 is the saturated vapor concentration (g/cm³), and L the soil column length (cm).

The solution to eq. (5) for the above initial and boundary conditions is given by eq. (20), which was derived from an equation given by Crank [24]:

$$\frac{G}{G_0} = 1 - \frac{x}{L} - \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin\left(\frac{n\pi x}{L}\right) \exp\left(\frac{-Dn^2\pi^2 t}{L^2}\right) \quad (20)$$

To fit the diffusion model (eq. 20) to the experimental data, the fitting criterion FMIN for all distances was minimized. FMIN is related to the sum of squares of deviations of measured from predicted G/G_0 ratios according to the following equation [25]:

$$\text{FMIN} = \left\{ \frac{1}{N} \sum_{i=1}^N \left[\left(\frac{G}{G_0} \right)_{mi} - \left(\frac{G}{G_0} \right)_{ci} \right]^2 \right\}^{0.5} \quad (21)$$

where N denotes the number of data points for all distances, $(G/G_0)_{mi}$ is the experimentally measured concentration ratio, and $(G/G_0)_{ci}$ the model computed concentration ratio.

The best fit retardation factor corresponded to the minimum value of the fitting criterion FMIN.

Results and discussion

Adequacy of the diffusion equation and local equilibrium

It was assumed that benzene volatilized from the reservoir (Fig. 1) and moved inside the soil column only by diffusion. Experimental profiles of vapor concentration with respect to time or distance were analyzed using eq. (20). The initial condition (eq. 17) was satisfied, because benzene-free soil ($G=0$) was used. Similarly, eq. (18) was valid, because measured vapor concentrations, G_0 , at sampling port #1 were constant within experimental error, after steady-state had been established, due to equilibrium with 200 mL of liquid benzene in the reservoir (Figs. 2 and 3). Equation (19) was valid, because of large volume dilution resulting from exposure of the column outlet in the atmosphere of a large (2.41 m × 1.62 m × 2.84 m) constant temperature room, which was continuously circulated by fans, providing a flow rate of 0.34 m³/s. Taking into account the air exchange in the room due to the door opening for sampling, checking room temperature and column condition, it was calculated that the steady-state benzene concentration in the room was below 0.03 mg/L. This value is higher than the actual benzene concentration in the room, because it did not take into account the amount of benzene sorbed by the soil. In any case, it is well below the GC detection limit, which was 3.0 mg/L at a sampling volume of 100 μL.

Vapor samples were taken from sampling ports #1, #3, #4, #5, and #6 (Fig. 1) and analyzed by GC. The vapor concentration, G , divided by the average concentration for the same day in sampling port #1, G_0 , was equal to the vapor concentration ratio, G/G_0 . The ratios were plotted as a function of

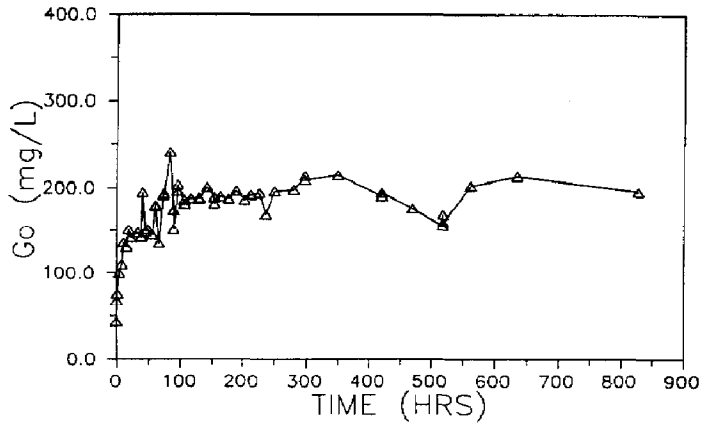


Fig. 2. Concentration of benzene vapor, G_0 , at the inlet ($x=0$) of the dry soil column.

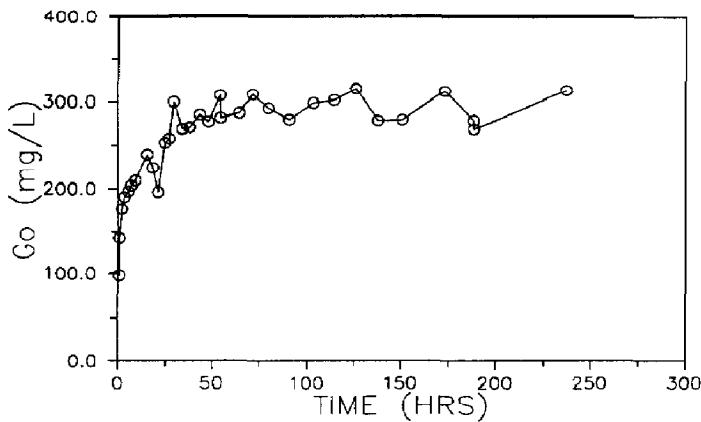


Fig. 3. Concentration of benzene vapor, G_0 , at the inlet ($x=0$) of the wet soil column.

time for sampling ports #3, #4, #5, and #6 and are shown in Figs. 4 and 5, for dry and wet soil, respectively. The solid lines in the figures are the best fit curves of eq. 20, superimposed on the experimental data points. Tables 1 and 3 list all input parameters that were used for model simulations.

Minimization of FMIN (eq. 21) for every individual distance from the column inlet resulted in R values slightly different for each distance (Table 4). This difference could be due to experimental error, slight heterogeneities within the system, or combination of both. In order to determine a single R value for each column, FMIN was minimized for the pooled data from all distances and resulted in $R=46$ for the dry soil (Fig. 4, Table 4) and $R=12$ for the wet soil column (Fig. 5, Table 4). To assess the goodness of fit of Fick's law to the experimental data, the means of residuals $[(G/G_0)_{mi} - (G/G_0)_{ci}]$ and FMIN values for each distance were computed and are listed in Table 4. Mean

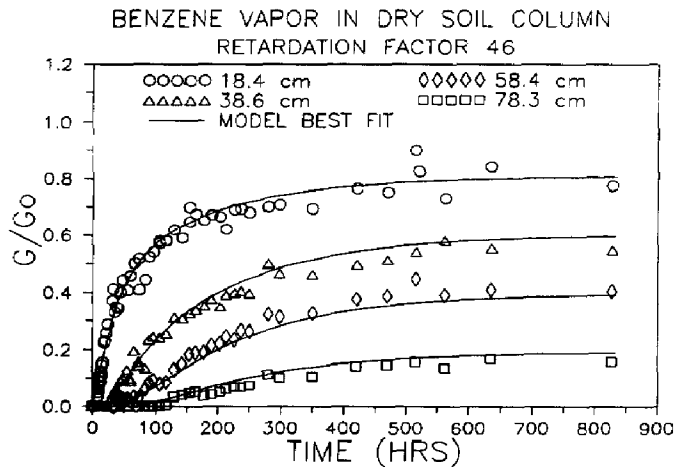


Fig. 4. Experimental and computed concentration profiles for benzene vapor in dry soil column.

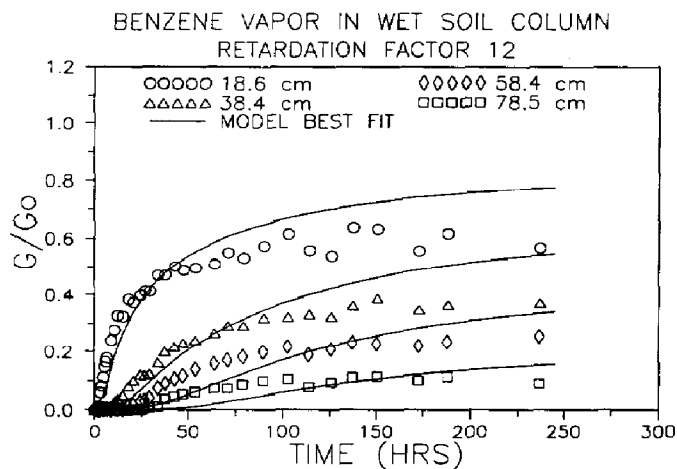


Fig. 5. Experimental and computed concentration profiles for benzene vapor in wet soil column.

residual values for both dry and wet soil columns were very close to zero, indicating that the model was not biased. FMIN values were smaller by more than a factor of 2 for the dry soil column, indicating a better model fit for the dry than the wet soil column. Visual inspection of Figs. 4 and 5 revealed a satisfactory fit for the dry soil and a rather poor one for the wet soil data.

The good agreement between eq. (20) and experimental data (Fig. 4) suggests that the diffusion equation was an adequate model in describing benzene vapor diffusion in dry soil. The local equilibrium assumption used to describe the vapor sorption by the soil was appropriate.

TABLE 4

Mean residual^a and FMIN values for benzene vapor in dry and wet soil

Dry soil				Wet soil			
Distance (cm)	Best fit <i>R</i>	Mean residual	FMIN	Distance (cm)	Best fit <i>R</i>	Mean residual	FMIN
18.4	46	0.00101	0.03637	18.6	13	0.00186	0.08402
38.6	48	0.00102	0.02169	38.4	14	-0.00918	0.05476
58.4	39	-0.00217	0.01396	58.4	11	-0.00735	0.03864
78.3	55	0.02561	0.008151	78.5	10	-0.00483	0.02390
Overall	46	0.00449	0.02484	Overall	12	-0.00465	0.05649

^a Residuals were computed from: $Res = [(G/G_o)_{mi} - (G/G_o)_{ei}]$.

The experimental data in Fig. 5 showed some early breakthrough, which may be indicative of a rate-limited mass exchange between the water and gas phases, followed by leveling off at lower than predicted concentrations, which may indicate biological degradation. Biological activity in the dry soil experiment was not significant, because the soil was treated by heating at 80 °C for 12 hours prior to exposure in benzene vapor. The wet soil columns, however, could support biological activity, under aerobic conditions, assuming that the organic soil could provide sufficient nutrients. Although it is very likely that biodegradation contributed to the poor model fit in Fig. 5, this does not constitute a proof, because the bacterial count of the soil and the oxygen consumption were not monitored throughout the experiment. The data analysis in Figs. 4 and 5 did not consider any density driven flow for benzene. This was based on identical concentration values from vapor samples obtained from the uppermost and lowermost points of the soil columns.

Figures 4 and 5 show that benzene concentrations reached steady-state after approximately 350 hours for the dry and 100 hours for the wet soil column. The average steady-state vapor concentration ratios \pm one standard deviation for ports #1, #3, #4, #5, and #6 for the dry soil column were: 1.0 ± 0.1 , 0.80 ± 0.07 , 0.55 ± 0.06 , 0.41 ± 0.03 , and 0.15 ± 0.02 , respectively. The respective concentration ratios for the wet soil column were: 1.0 ± 0.06 , 0.59 ± 0.01 , 0.35 ± 0.04 , 0.22 ± 0.02 , and 0.10 ± 0.008 . As the distance from the source (port #1) increased, vapor concentration decreased. This can be explained on the basis of eq. (5), which at steady-state becomes:

$$\frac{d^2G}{dx^2} = 0 \quad (22)$$

Using the boundary conditions (eqs. 18, 19), the solution of eq. (22) is:

$$G = G_0 \left(1 - \frac{x}{L} \right) \quad (23)$$

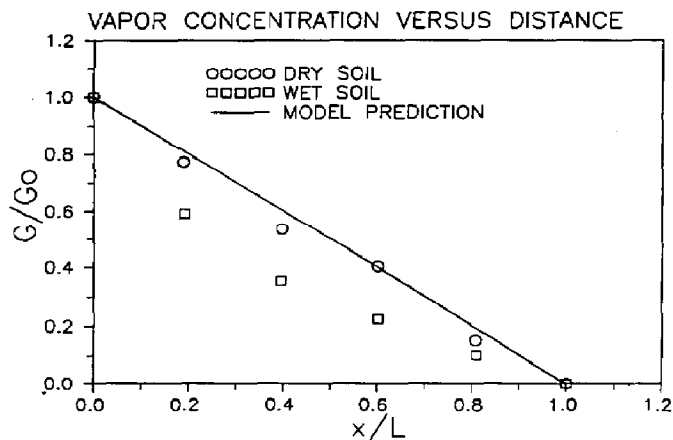


Fig. 6. Steady-state concentration profiles of benzene vapor versus distance for dry and wet soil columns.

Figure 6 shows that the concentration at steady-state decreased linearly with increasing distance in the dry soil column, in agreement with eq. (23). In the wet soil column, the concentration decrease with distance was not linear, probably because of benzene vapor biodegradation (Fig. 5). Field scale biodegradation of vapors in unsaturated soil was also reported by Ostendorf and Kampbell [26]. The concentration ratio, G/G_0 , for the wet soil column did not increase much between 100 and 250 hours and averaged at approximately 0.6 at the distance of 18.6 cm. The theoretical concentration ratio at steady-state at the same distance, based on Fick's law, should be equal to 0.81, however.

The tortuosity values used in this study were determined according to eqs. (9) and (10) and were applied to all experimental data simulations. An error in the estimate of tortuosity would be reflected in the values of D_w and D_a (eqs. 7 and 8). A sensitivity analysis for τ_w in the 0.1–0.9 range showed no difference in the computed concentration profiles, indicating that eq. (20) is insensitive to τ_w . A sensitivity analysis for τ_a in the 0.1–0.9 range is presented in Fig. 7 for the dry soil column. Increase of τ_a by 25% ($\tau_a = 0.916$) resulted in small difference in the computed concentration versus time curve. In contrast, decrease of τ_a by 25% ($\tau_a = 0.550$) or 50% ($\tau_a = 0.367$) resulted in a much larger difference in the same curve, indicating that the diffusion model was more sensitive to $\tau_a < 0.733$ (computed from eq. 10). Sensitivity analysis for the wet soil column was not conducted because of the poor model fit.

The experimental data of the dry soil column at $x = 58.4$ cm, were compared with model predictions (eq. 20) for different R values, in Fig. 8. The results showed that the diffusion model was very sensitive with respect to R at low R values ($R < 30$) and less sensitive at higher R values ($R > 40$). Sensitivity analysis for the wet soil column was not conducted because of the poor model fit.

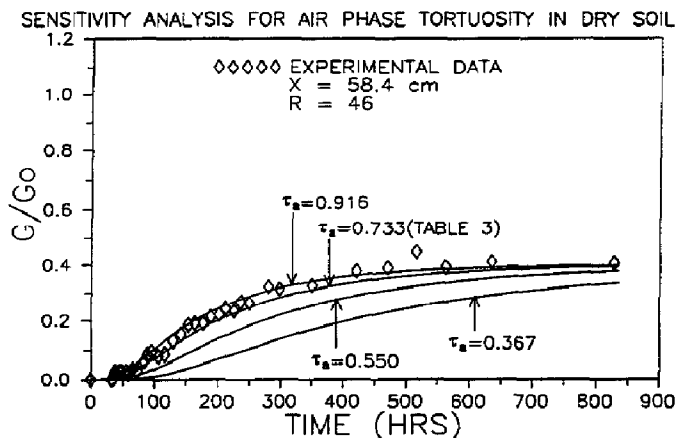


Fig. 7. Sensitivity analysis of benzene vapor in dry soil for different values of air-phase tortuosity.

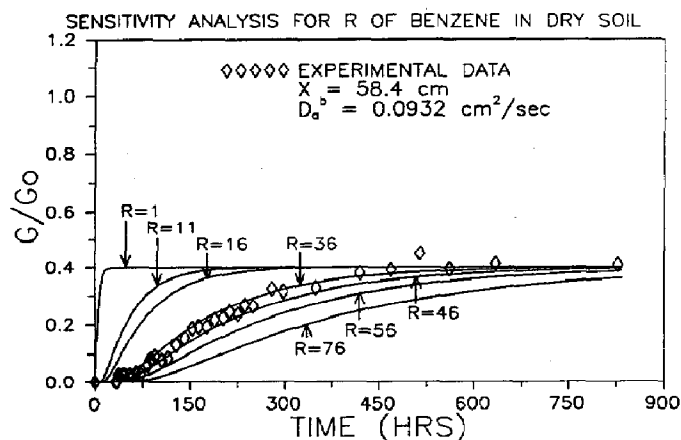


Fig. 8. Sensitivity analysis of benzene vapor in dry soil for different values of retardation factor.

Sorption coefficients

The best fit retardation factors of benzene vapor were 46 and 12 for dry and wet soil, respectively. This is consistent with results from previous studies, which showed a significant reduction in sorption capacity with increasing moisture because of competition by water molecules [27]. A lower sorption capacity for benzene would result in a smaller K_{obs} value for wet soil, or a smaller R , according to eq. (12).

The best fit retardation factors were used to calculate an overall sorption coefficient, K_{obs} , using eq. (12). K_{obs} values of benzene for dry and wet soil were 12 and 1.9 cm^3/g , respectively. For the dry soil area of 1.45 m^2/g , bulk density of 1.5 g/cm^3 (Table 1), and water surface area of 11.4 $\text{\AA}^2/\text{molecule}$ [28], a moisture content required for monolayer coverage of the soil of 0.00057 $\text{mL H}_2\text{O}/\text{cm}^3$ of

TABLE 5

Vapor phase sorption coefficients from column experiments

Soil	R	K_{obs} (cm ³ /g)	K'_d ^a (cm ³ /g)	K_d ^a (cm ³ /g)
Dry	46	12	5.3	1.2 ^b
Wet	12	1.9	0	0.35

^a Computed from eq. (14).^b Computed from eq. (15).

soil was calculated. For $\varepsilon_w = 0.001$, the overall coverage of dry soil was less than two layers of water molecules. To calculate the benzene gas phase sorption coefficient, K'_d , from K_{obs} , at this water coverage, eq. (14) was used, which assumes no effect of moisture content on K_d , even at very low moisture contents. Therefore, a saturated system $K_d = K_{oc} f_{oc} = 1.23 \text{ cm}^3/\text{g}$ was used, where $K_{oc} = 80 \text{ cm}^3/\text{g}$ [29] and $f_{oc} = 0.0154$ (Table 1). Thus, the gas phase sorption coefficient for the dry soil column was calculated as $5.3 \text{ cm}^3/\text{g}$ (Table 5). For the wet soil, $K'_d = 0$ [14, 15]. Therefore, $K_d = K_{obs} K_H = 0.35 \text{ cm}^3/\text{g}$. This would correspond, however, to a $K_{oc} = 0.35/0.0154 \approx 23 \text{ cm}^3/\text{g}$, almost four times lower than the $K_{oc} = 80 \text{ cm}^3/\text{g}$ reported [29]. This difference, however, is within the expected accuracy of eq. (15).

Conclusions

The results of this study showed that the diffusion equation, accounting for water phase partitioning and linear sorption isotherm, adequately described the experimental concentration profiles of benzene vapor in a dry soil column. However, its applicability to benzene vapor in the wet soil column resulted in poor data fit, which was attributed to possible biodegradation [26]. Due to experimental difficulties, the assumption of isotherm linearity could not be independently confirmed. However, linear isotherms are expected in wet soil systems and, in general, at low vapor concentrations [27].

Best fit retardation factors for benzene vapor were 46 and 12 for the dry and wet soil column, respectively. The lower R value for the wet soil column is consistent with results from previous studies, which showed a significant reduction in sorption capacity with increasing moisture, because of competition by water molecules [27]. The higher sorption capacity for benzene vapor in dry soil resulted in a higher K_{obs} value or larger R , according to eq. (12). However, because of the poor fit of diffusion equation to experimental data, it was not possible to determine a reliable K_{obs} value for wet soil, and the retardation factor ($R = 12$) must be used with caution. Sensitivity analysis of the diffusion model was performed only on dry soil and showed that the model

was very sensitive with respect to R for low R values ($R < 30$), and less sensitive for high R values ($R > 40$). It was also very sensitive with respect to τ_a for $\tau_a < 0.733$ and less sensitive for $\tau_a > 0.733$.

Acknowledgments

We thank Mr. Allen Rigdon, scientist of the Soil Conservation Service, Waycross, Georgia, for assisting us in soil collection. We also thank Dr. A. Horowitz of U.S.G.S., Doraville, Georgia, for determining the soil surface area.

References

- 1 W.A. Jury, W.F. Spenser and W.F. Farmer, Behavior assessment model for trace organics in soil, I, Model description, *J. Environ. Qual.*, 12(4) (1983) 558–564.
- 2 A.L. Baehr and M.Y. Corapcioglu, A compositional multiphase model for groundwater contamination by petroleum products, 2, Numerical solution, *Water Resour. Res.*, 23(1) (1987) 201–213.
- 3 A.L. Baehr, Selective transport of hydrocarbons in the unsaturated zone due to aqueous and vapor phase partitioning, *Water Resour. Res.*, 23(10) (1987) 1926–1938.
- 4 C.A. Shoemaker, T.B. Culver, L.W. Lion and M.G. Peterson, Analytical models of the impact of two-phase sorption on subsurface transport of volatile chemicals, *Water Resour. Res.*, 26(4) (1990) 745–758.
- 5 T.B. Culver, C.A. Shoemaker and L.W. Lion, Impact of vapor sorption on the subsurface transport of volatile organic compounds: A numerical model and analysis, *Water Resour. Res.*, 27(9) (1991) 2259–2270.
- 6 B.E. Sleep and J.F. Sykes, Modeling the transport of volatile organics in variably saturated media, *Water Resour. Res.*, 25(1) (1989) 81–92.
- 7 A.A. Karimi, W.J. Farmer and M.M. Cliath, Vapor-phase diffusion of benzene in soil, *J. Environ. Qual.*, 16(1) (1987) 38–43.
- 8 W.J. Farmer, M.S. Yang, J. Letey and W.F. Spencer, Hexachlorobenzene: Its vapor pressure and vapor phase diffusion in soil, *Soil Sci. Soc. Am. J.*, 44 (1980) 676–680.
- 9 Ts. Galin, Z. Gerstl and B. Yaron, Soil pollution by petroleum products, III. Kerosene stability in soil columns as affected by volatilization, *J. Contam. Hydrol.*, 5 (1990) 375–385.
- 10 ASTM, Standard method for particle-size analysis of soils, In: *Annual Book of ASTM Standards, Part 19, Natural Building Stones; Soil and Rock; Peats, Mosses, and Humus*. American Society for Testing and Materials, Philadelphia, PA, 1979, pp. 112–122.
- 11 W.H. Gardner, Water content, In: A. Klute (Ed.), *Methods of Soil Analysis, Part 1, Physical and Mineralogical Methods*. American Society of Agronomy, 2nd edn., Madison, WI, 1986.
- 12 G.R. Blake and K.H. Hartge, Particle density, In: A. Klute (Ed.), *Methods of Soil Analysis, Part 1, Physical and Mineralogical Methods*. American Society of Agronomy, 2nd edn., Madison, WI, 1986.
- 13 A. Horowitz and K. Elrick, The relation of stream sediment surface area, grain size and composition to trace element chemistry, *Appl. Geochem.*, 2 (1987) 437–451.
- 14 S.K. Ong and L.W. Lion, Effects of soil properties and moisture on the sorption of trichloroethylene vapor, *Water Res.*, 25(1) (1991) 29–36.
- 15 S.K. Ong and L.W. Lion, Mechanisms for trichloroethylene vapor sorption onto soil minerals, *J. Environ. Qual.*, 20 (1991) 180–188.

- 16 P.A. Ryan and Y. Cohen, Diffusion of sorbed solutes in gas and liquid phases of low-moisture soils, *Soil Sci. Soc. Am. J.*, 54 (1990) 341–346.
- 17 G.P. Curtis, M. Reinhard and P.V. Roberts, Sorption of hydrophobic organic compounds by sediments, In: J.A. Davis and K.F. Hayes (Eds.), *ACS Symp. Series 323, Geochemical Processes at Mineral Surfaces*, 1986, pp. 191–216.
- 18 D. Mackay and W. Y. Shiu, A critical review of Henry's law constants for chemicals of environmental interest, *J. Phys. Chem. Ref. Data*, 10(4) (1981) 1175–1199.
- 19 R.C. Weast (Ed.) *CRC Handbook of Chemistry and Physics*, 66th edn. CRC Press, Boca Raton, FL, 1985.
- 20 D. Mackay, W.Y. Shiu and R.P. Sutherland, Determination of air–water Henry's law constants for hydrophobic pollutants, *Environ. Sci. Technol.*, 13(3) (1979) 333–337.
- 21 R.J. Millington and J.P. Quirk, Permeability of porous solids, *Trans. Faraday Soc.*, 57 (1961) 1200–1207.
- 22 G.A. Lugg, Diffusion coefficients of some organic and other vapors in air, *Anal. Chem.*, 40(7) (1968) 1072–1077.
- 23 W.J. Lyman, W.F. Reehl and D.H. Rosenblatt, *Handbook of Chemical Property Estimation Methods*. McGraw-Hill, New York, 1982.
- 24 J. Crank, *The Mathematics of Diffusion*, 2nd edn. Clarendon Press, Oxford, 1975.
- 25 W.E. Thacker, V.L. Snoeyink and J.C. Crittenden, Modeling of activated carbon and coal gasification char adsorbents in single-solute and bisolute systems, *Water Resources Research Report 161*, University of Illinois, Urbana, IL, 1981.
- 26 D.W. Ostendorf and D.H. Kampbell, Biodegradation of hydrocarbon vapors in the unsaturated zone, *Water Resour. Res.*, 27(4) (1991) 453–462.
- 27 C.T. Chiou and T.D. Shoup, Soil sorption of organic vapors and effects of humidity on sorptive mechanism and capacity, *Environ. Sci. Technol.*, 19 (1985) 1196–1200.
- 28 M.S. Peterson, L.W. Lion and C.A. Shoemaker, Influence of vapor phase sorption and diffusion on the fate of trichloroethylene in an unsaturated aquifer system, *Environ. Sci. Technol.*, 22 (1988) 571–578.
- 29 W.A. Jury, D. Russo, G. Streile and H. El Abd, Evaluation of volatilization by organic chemicals residing below the soil surface, *Water Resour. Res.*, 26(1) (1990) 13–20.