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## Transport and fate of volatile organic chemicals in unsaturated, nonisothermal, salty porous media: 2. Experimental and numerical studies for benzene

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### Abstract

Simultaneous transport in soil of heat, water, potassium chloride, and benzene was studied experimentally and numerically. A laboratory experiment permitted observation of temperature, water content, chloride concentration and benzene concentration distributions in soil. A numerical model based upon newly developed transport theory was used to simulate the observed data. Transport of benzene in soils was simulated numerically under isothermal and nonisothermal conditions. Simulated results for benzene were compared with experimental data. Experiments were conducted in sealed aluminum columns (0.05-m I.D. and 0.20-m length) with sterilized salinized unsaturated Fayette soil. The soil had initial water content of 0.22 m<sup>3</sup>/m<sup>3</sup> and initial inorganic solute concentration of 0.20 mol/kg. Benzene was injected at one end of each soil column (top end) to provide 143 g/m<sup>3</sup> benzene in the upper 0.01 m portion. The isothermal soil columns were set in an incubator at 29°C. The nonisothermal experiment had upper and lower boundary temperatures of 34 and 21°C, respectively. Isothermal and nonisothermal experiments each lasted for seven days. A numerical model based upon heat and mass transfer theory was used to predict transient soil temperature, water content, and inorganic and organic chemical distributions. Both predicted and measured final temperatures showed linear distributions. In the non-isothermal study, water moved from the hot region toward the cold region, and inorganic solute accumulated in the hot region. Benzene redistributed along the soil column for both isothermal and nonisothermal conditions. Total concentration of benzene in the cold region under nonisothermal conditions was larger than the concentration of benzene in the hot region. On the other hand, the concentration of total benzene was approximately uniform along the soil column under isothermal conditions. For isothermal conditions, the benzene concentration by volume in the three phases followed the order: liquid > solid > gas. The results of this study indicated that transport

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models need to include the effect of temperature and temperature gradient to describe the movement of volatile chemicals in soils. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Predicting volatile organic chemical (VOC) transport in contaminated soils is essential in risk assessment for groundwater contamination, as well as for remediation of contaminated sites by vapor phase extraction methods. Furthermore, biodegradation of VOC in unsaturated soils is dependent on optimizing the factors that affect microbial growth: water, heat, and inorganic nutrients. Thus, a model that couples water, heat, and inorganic solute movement with VOC transport in unsaturated soils may aid in developing better bioremediation strategies. Nassar and Horton [1] recently developed a new theory of heat, water, inorganic solute, and VOC transport in unsaturated soils. To validate this theory, simulated data need to be compared with experimentally measured transport of a representative VOC under isothermal and nonisothermal conditions. Benzene was chosen as a representative VOC because it has a relatively large water solubility (1780 mg/l), large vapor density (325 mg/l), and can be adsorbed by soil [2]. Benzene is a known carcinogen and an ubiquitous pollutant that poses a threat to ground and surface water.

Most of the previous research was focused on the movement of benzene in porous media under isothermal conditions. These studies considered Fickian diffusion to be the primary mechanism for benzene movement [3–5]. Karimi et al. [3] stated that the steady-state vapor diffusion of benzene in soil under isothermal conditions with negligible water flow was directly related to the soil air-filled porosity. The volatilization flux of benzene through a soil surface was greatly reduced by increased soil bulk density and increased soil–water content. Lin and Hildemann [4] presented numerical results of benzene volatilization under isothermal conditions. They stated that 80% of the benzene in their conceptualized landfill partitioned to the solid phase, 17% to the liquid phase, and approximately 3% to the gas phase. They found that migration of benzene in the liquid phase was slow because of retardation caused by adsorption: the leachate was moving .05 m/d. Voudrias and Li [5] studied isothermal diffusion of benzene in dry (moisture content of  $0.001 \text{ m}^3/\text{m}^3$ ) and wet soils (moisture content of  $0.124 \text{ m}^3/\text{m}^3$ ). They found that diffusion with equilibrium partitioning adequately described vapor transport in dry soil. In the wet soil, the model overestimated benzene movement when compared with observed values. The authors attributed this overestimation to the biodegradation of benzene in the wet soil.

Few recent studies have considered the effect of temperature on the transport of benzene in unsaturated soil [6–8]. These researchers included the effect of temperature via the transport coefficients of benzene. Nair et al. [8] reported that neglecting gas-phase diffusion in the unsaturated zone during the leaching of benzene can result in an underestimation of benzene leaching rate to ground water. Cohen and Ryan [6] reported that the diurnal fluctuations of temperature should be considered for estimating

the volatilization rate of contaminant from the soil surface. Cohen et al. [7] proposed a one-dimensional model that considered the effect of natural convection, and the variation of diffusivity and vapor phase adsorption with temperature on benzene fluxes across the soil–air interface. Their study indicated that natural convection effects were not noticeable. Diurnal temperature changes were found to lead to fluctuations in the concentration profiles and the volatilization fluxes. The thermal adsorption–desorption of benzene on soil matrices was studied by Wu and Bozzelli [9]. They reported that equilibrium constants were strongly dependent on temperature, but not on particle size.

Benzene movement in soil has rarely been studied experimentally under nonisothermal conditions [6–8]. The first objective of this study was to perform isothermal and nonisothermal experiments to observe heat, water, inorganic chemical, and benzene transfer in unsaturated soil. The second objective was to test the heat and mass transfer theory introduced by Nassar and Horton [1] under isothermal and nonisothermal conditions. The theory describes the fate and transport of VOC in unsaturated, non-isothermal, salinized soil.

## 2. Materials and methods

### 2.1. Experimental

Subsurface soil materials were collected from Iowa loess deposits (Fayette series silty clay loam with 35% clay, 8% sand, and 57% silt material; Unified classification: CL; AASHTO classification: A-6). The soil materials were obtained by excavation, then air-dried and ground to pass a 2-mm sieve. The resulting soil materials were wetted with a potassium chloride solution to obtain an initial volumetric water content of 0.215  $\text{m}^3/\text{m}^3$  and an initial solute concentration of 0.20 mol/kg. The moistened soil was covered and stored at 20°C for about 4 days, then sterilized by using a gamma radiation technique (a dose of 53.9 KGy). The soil was sterilized to avoid or minimize microbial degradation of benzene.

Aluminum cylinders (5.0-cm ID and 20-cm high) were predrilled each 0.02 m increment. The resulting holes were fitted with Teflon-coated butyl septa and sealed with epoxy. These septa were used as ports for collecting gas samples of benzene at the termination of each experiment. The cylinders were sterilized and packed with the sterilized soil. Each soil column was closed at both ends with epoxy-sealed aluminum covers. A column leak test for benzene, performed on a sealed cylinder containing no soil, showed that the loss of benzene was less than 5% after 10 days of equilibration at 25°C. A volume of 7  $\mu\text{l}$  of benzene was injected in the top 0.01-m layer of each soil column to obtain 143  $\text{g}/\text{m}^3$  in soil solution as an initial total concentration. The bulk densities of the soil columns were approximately 1200  $\text{kg}/\text{m}^3$ . Two experiments were performed: a nonisothermal experiment and an isothermal experiment. Three soil columns were prepared as replicates for the nonisothermal treatment, and two soil columns were prepared as replicates for the isothermal treatment.

For the nonisothermal experiment, eight type-T thermocouples (Copper-Constantan) were used to measure the temperature of the soil at different locations of the column

axis. Thermocouples were used to measure the boundary temperatures (at depths of 0.00 and 0.20 m), and the other six thermocouples were inserted at depths of 0.02, 0.04, 0.08, 0.12, 0.160, and 0.18 m measured from the top end of each column. Soil temperatures were recorded hourly by a CR5 digital recorder (Campbell Scientific, Logan, UT). The three soil columns used in the nonisothermal studies were buried vertically within a large soil bin (0.50-m in diameter). Soil was placed around each column to insulate each soil column against heat transfer in the radial direction. A schematic of the nonisothermal experimental set up for a soil column is presented (Fig. 1). Following benzene injection, columns were equilibrated for 7 days. In the nonisothermal columns, the upper boundary temperatures were controlled at a constant temperature of 33–35°C with thermal irradiation of the top of the soil column. For this purpose, a 350 W tungsten lamp together with a reflector was positioned 0.25 m directly above the bin soil surface to obtain a nearly uniform heat flux distribution. The lower boundary temperature of 21–22°C was achieved by circulating constant temperature water at the bottom of the soil columns. For the isothermal experiments, the two columns were maintained in an incubator at 29°C for 7 days.

At the end of the experiment, the soil columns were removed from the bin or from the incubator. Gas samples of benzene were obtained from each soil column by using a gas-tight syringe. The syringe needle was inserted into the column through each septum, and 250- $\mu$ L gas samples of soil air were obtained. The gas samples were analyzed by gas chromatography by using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector and a DB-624 column (0.53 mm i.d.  $\times$  30 m, J&W

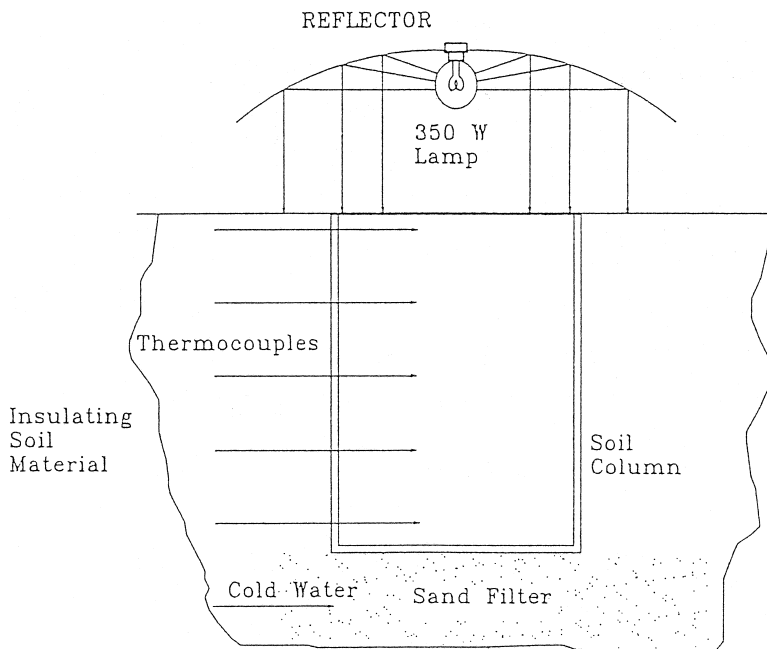


Fig. 1. Schematic diagram for the nonisothermal experiment set-up.

Scientific). The column temperature was 120°C, injector and detector temperatures were 200°C, and the carrier gas was He. The peak quantification was done by using external gas standards. After obtaining gas samples each soil column was sectioned to determine soil water content and inorganic solute distributions. Values of inorganic solute concentration were estimated by determining chloride concentration in soil-water extracts of 1:2 from each soil sample.

## 2.2. Theoretical analysis

The theory developed by Nassar and Horton [1] for heat, water, and inorganic solute and VOC transfer was used for the present analysis. The theory considers that water (vapor and liquid phases) moves in response to gradients of temperature, soil water matric potential, and solution osmotic potential and gravity potential. Heat transfer occurs by conduction, and both latent heat and sensible heat convection. The inorganic solute moves by mass flow of water (convective flow), diffusion–dispersion, and salt-sieving. The VOC moves in vapor phase by isothermal and nonisothermal diffusion and moves in liquid phase by diffusion–dispersion and convection.

### 2.2.1. Governing equations

Solving the following equations will describe temporal and spatial variations of soil temperature, water content, inorganic solute concentration and volatile organic solute concentration in vertical soil columns. Assuming one-dimensional transfer in the  $z$  direction, the nonsteady-state heat transfer equation can be written as

$$K_1 \frac{\partial T}{\partial t} + K_2 \frac{\partial \theta}{\partial t} + K_3 \frac{\partial C}{\partial T} = -\nabla q_h \quad (1)$$

where  $q_h$  is the net heat flux ( $\text{W}/\text{m}^2$ ); the coefficients  $K_1$ ,  $K_2$ , and  $K_3$  are storage terms for heat; and  $\theta$  ( $\text{m}^3/\text{m}^3$ ),  $T$  ( $^\circ\text{C}$ ), and  $C$  ( $\text{mol}/\text{kg}$ ) are water content, temperature, and inorganic solute concentration, respectively.

The transient equation for soil water flow can be written as

$$\alpha_1 \frac{\partial \theta}{\partial t} + \alpha_2 \frac{\partial C}{\partial t} + \alpha_3 \frac{\partial T}{\partial t} = -\nabla \left( \frac{q_v}{\rho_w} + \frac{q_L}{\rho_L} \right) \quad (2)$$

where  $q_v$  and  $q_L$  are the mass fluxes of vapor and soil water, respectively, ( $\text{kg}/\text{m}^2\text{s}$ );  $\rho_w$  and  $\rho_L$  are the density of pure water and soil solution, respectively, [ $\text{kg}/\text{m}^3$ ]; and  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$  are storage terms for water.

The nonsteady-state equation for inorganic solute transport can be written as

$$\frac{\partial(C\theta)}{\partial t} = -\nabla \left( \frac{n_c}{\rho_L} \right) \quad (3)$$

where  $n_c$  is the net flux of solute ( $\text{mol}/\text{m}^2 \text{ s}$ ).

The mass balance of volatile organic compounds can be described [1] as

$$\frac{\partial(C_i \theta)}{\partial t} = -\nabla q_o \quad (4)$$

where  $q_o$  is net organic chemical flux, ( $\text{mol}/\text{m}^2 \text{ s}$ ); and  $C_i$  is the organic chemical concentration ( $\text{mol}/\text{kg}$ ). Benzene degradation was assumed to be negligible because the soil was sterilized and the experiment was not lengthy. The range of temperature used in the present study was 21 to 34°C. Significant convective transfer of gas phase for benzene cannot occur in this range of temperature. Therefore, the mechanisms of benzene movement under the conditions of this study were diffusion in both liquid and gas phases and by convection in the liquid phase.

### 2.2.2. Initial and boundary condition

The initial conditions associated with Eqs. (1)–(4) are given by

$$\begin{aligned} T(z,0) &= T_i, \quad \theta(z,0) = \theta_i, \quad C(z,0) = C_i, \quad (0 < z < 1), \\ C_i(z,0) &= C_o \quad (0 < z < 0.01 \text{ m}), \quad \text{and} \\ C_i(z,0) &= 0.0 \quad (0.01 < z < 1) \end{aligned} \quad (5)$$

where 1 is soil column length (m).

The temperature boundary conditions at both ends of the closed soil columns in Fig. 1 can be described by

$$T(0,t) = T_h \quad t > 0 \quad (6)$$

$$T(1,t) = T_c \quad t > 0 \quad (7)$$

The boundary conditions for water and solute are given in terms of net mass fluxes by

$$(q_1 + q_v)(0,t) = 0, \quad n_c(0,t) = 0, \quad q_o(0,t) = 0 \quad t > 0 \quad (8)$$

$$(q_1 + q_v)(1,t) = 0, \quad n_c(1,t) = 0, \quad q_o(1,t) = 0 \quad t > 0 \quad (9)$$

### 2.2.3. Soil transport properties and parameters

The water, heat, and inorganic chemical transfer properties were described in detail [10], and the organic chemical transport and partitioning coefficients were described in [1]. Partition coefficients (solid/vapor) for benzene were measured at five moisture contents by the equilibrium partitioning in closed systems (EPICS) headspace technique [11,12]. Briefly, the soil materials (5 to 20 g) with a pre-adjusted moisture content were placed into 60-ml amber serum bottles and crimped-sealed with Teflon-coated butyl septa. Benzene was applied to the bottles by using a gas-tight syringe to exchange 1 ml of air with 1 ml of a saturated benzene vapor. The bottles were equilibrated on a rotator for 24 h, after which 1 ml of headspace was analyzed for benzene concentration by gas chromatography. The isotherms were linear and the solid/vapor partition coefficients,

$K_{sg}$  ( $\text{m}^3 \text{kg}^{-1}$ ) were determined by plotting the left hand side of Eq. (10) vs.  $M/V_S$  [11]:

$$\frac{V_B C_B}{V_S C_S} = K_{sg} \frac{M}{V_S} \quad (10)$$

where  $V_B$  and  $C_B$  are the gas volume and concentration of benzene in the bottles without soil,  $V_S$  and  $C_S$  are the gas volume and concentration of benzene in the bottles with soil, and  $M$  is mass of soil. Fig. 2 shows measured values for partitioning coefficient ( $K_{sg}$ ) for Fayette soil as a function of water content. The solid/water partition coefficient,  $K_{sl}$ , for benzene was determined by fitting Eq. (11) to the plot of  $K_{sg}$  vs. moisture content of the soil (Fig. 2):

$$K_{sg} = \frac{K_{sl}}{K_{gl}} + \frac{\omega}{K_H \gamma \rho_w} \quad (11)$$

where  $\omega$  is the water content of soil (kg  $\text{H}_2\text{O}$  per kg soil),  $\gamma$  is the activity coefficient of benzene in water (assumed to be 1; [11,13]), and  $\rho_w$  is the density of water. Eq. (11)

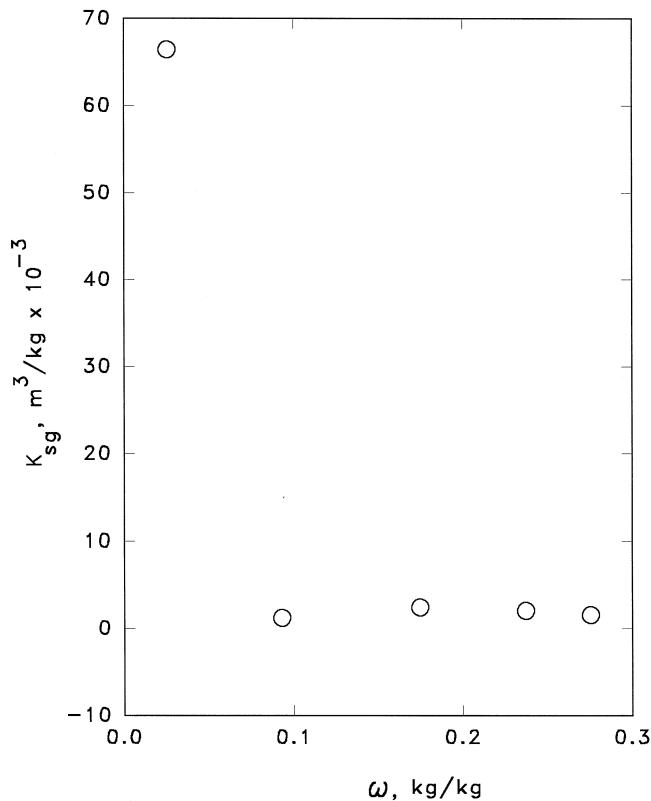


Fig. 2. Measured adsorption coefficient,  $K_{sg}$ , (solid/vapor) for Fayette soil.

indicates that the  $K_{sl}$  of benzene can be determined from the intercept of the  $K_{sg}$  vs. moisture content relationship. The  $K_{sl}$  value for Fayette soil was found to be  $0.343 \times 10^{-3} \text{ m}^3/\text{kg}$ . The  $K_{sl}$  and  $K_{sg}$  values were used to estimate the amount of benzene in liquid and solid phases from the measured gas phase concentration. For the temperature range used in the column experiments, the effect of temperature on the partition coefficients ( $K_{sl}$  and  $K_{sg}$ ) and the solubility of benzene could be neglected [14].

The temperature- and relative humidity-corrected Henry's law constant was calculated [15] as:

$$K_{gl} = \frac{Mp^s h}{RTC_w} \quad (12)$$

where  $M$  is the molecular weight of benzene (kg/mol),  $p^s$  is the saturated vapor pressure (MPa),  $h$  is the relative humidity (dimensionless),  $R$  the universal gas constant ( $\text{m}^3 \text{ Mpa}/\text{mol K}$ ),  $T$  is the absolute temperature (K), and  $C_w$  is the solubility of benzene ( $\text{kg}/\text{m}^3$ ). The Henry's law constant that describes the partitioning between the gas and liquid phases is shown in Fig. 3. It ranged from 0.20 to 0.33 under the temperature range and relative humidity of this study.

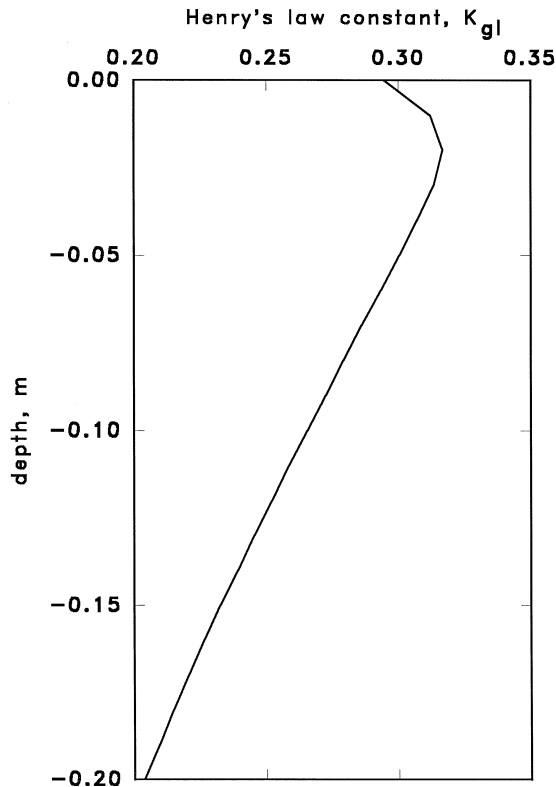


Fig. 3. Calculated Henry's law constant,  $K_{gl}$ , using Eq. (12).



#### 2.2.4. Numerical solution procedure

An implicit finite difference numerical scheme was used to solve the four partial differential equations (PDE) [(1), (2), (3), and (4)] by using a backward difference formula for the time derivative. Using this scheme, the value of any variable ( $T$ ,  $\theta$ ,  $C$ , or  $C_i$ ) at a given time  $t + \Delta t$  was a function of the values of the variables at the preceding time,  $t$ , and the values of all variables at the same time,  $t + \Delta t$ . A simple linearized finite difference form of the PDE was obtained by including coefficients estimated as the arithmetic mean of their values at two adjacent nodes or at two consecutive times. The resulting system of finite difference equations with  $4N$  unknowns was solved simultaneously for each time step, where  $N$  was the number of nodes along the soil column axis. An iterative method was used when solving these equations after arranging them in matrix form. The  $4N \times 4N$  coefficient matrix was block-tridiagonal, and was efficiently solved by using the Gaussian elimination method. For a given time instant of order  $j + 1$ , the values of the matrix coefficients were first taken as those for the preceding time instant of order  $j$ . Then, a first approximation of values of the  $4N$  variables for the given time instant was obtained. These values were introduced to improve the matrix coefficients and then to obtain new values of the variables. Proceeding in a similar manner, a final solution could be obtained for the given time instant of order  $j + 1$  with an arbitrarily chosen accuracy of each variable.

#### 2.2.5. Model evaluation

The model's ability to predict a variable was evaluated. Visual comparison of simulated and observed data provided a quick and often comprehensive means of assessing the accuracy of the model prediction. However, quantitative evaluation of the model was also included. Mean error (ME) and root mean square error (RMSE) were used as criteria for evaluating the model [16]. The ME values were estimated as:

$$\text{ME} = \frac{1}{N} \sum (V_p - V_m) \quad (13)$$

and RMSE was estimated as:

$$\text{RMSE} = \left( \frac{1}{N} \sum (V_p - V_m)^2 \right)^{1/2} \quad (14)$$

$V_m$  is the observed value of a variable ( $T$ ,  $\theta$ ,  $C$ , or concentration of benzene in gas phase),  $V_p$  is the predicted value of a variable, and  $N$  is number of observations for the variable.

### 3. Results and discussion

The predicted and measured temperature and soil water content distributions in nonisothermal columns are shown in Figs. 4 and 5, respectively. Whereas the observed temperature distributions compared favorably with the model predictions, the predicted water content distributions matched the observed values only in trend. The net water

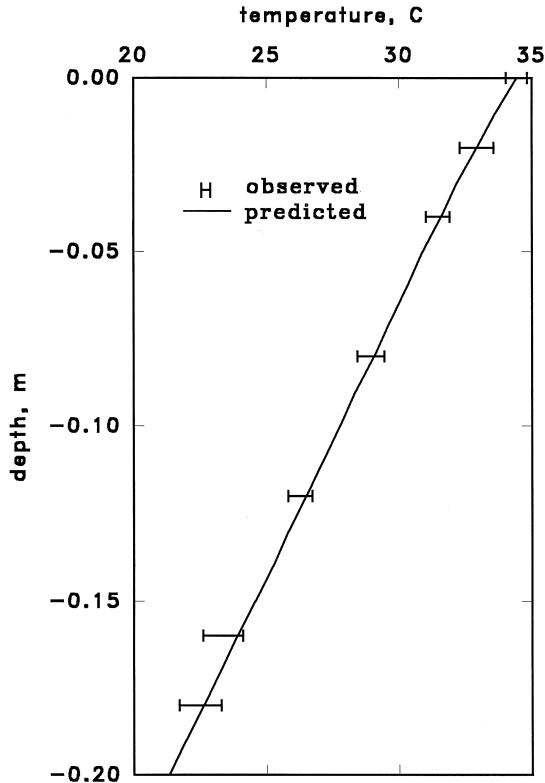


Fig. 4. Measured and predicted temperature distribution for the nonisothermal experiment.

transfer to the lower half of the soil column (the wet region) was greater than predicted. The deviation between the predicted and observed water distributions could have been the result of the overprediction of liquid water transfer from the cold end of the column toward the hot end, or the underestimation of water vapor transfer from the hot end toward the cold end. Because vapor and liquid coefficients were estimated from theory, it was not clear whether vapor flow was underestimated or whether liquid flow was overestimated.

Predicted and measured soil solution chloride concentration distributions are shown in Fig. 6a. In general, the proposed model performs well in predicting chloride concentration distributions at the water contents used in the present study. The observed and predicted values indicated large concentration gradients at both boundaries. Fig. 6b shows the predicted solute concentration based upon the mass of solid phase. The accumulation of solute in the hot soil revealed that convective solute transfer toward the hot soil was greater than diffusive solute transfer toward the cold soil. For the solute to accumulate, convection of solute toward the warm region should exceed diffusion of solute away from the warm region. However, at the hot end of soil columns, the predicted solute concentrations was less than the observed values. Underestimating salt

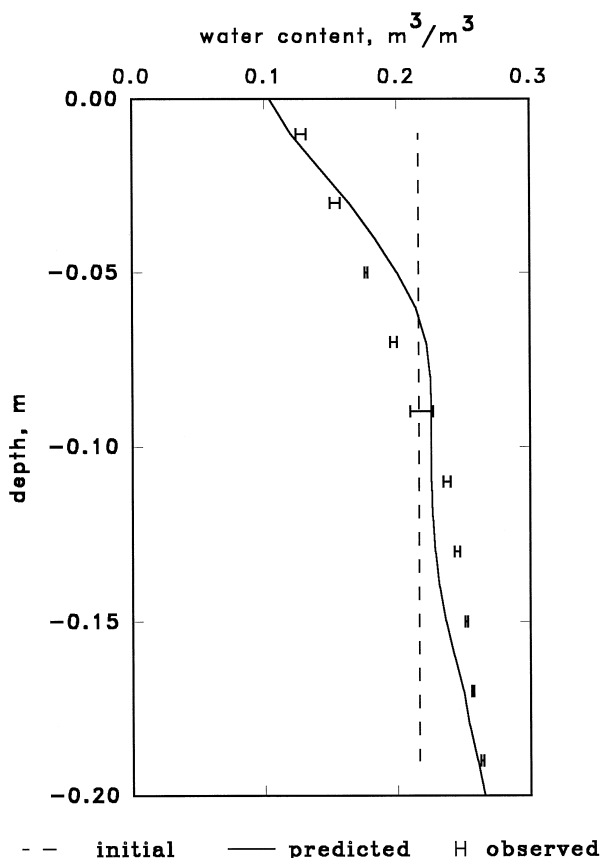


Fig. 5. Measured and predicted soil water content distributions, and initial soil water content for the nonisothermal experiment.

concentration at the hot ends may have resulted from a combination of factors. If evaporation was underestimated as suggested by the water distribution data (Fig. 5), the solute would not concentrate as much at the hot end. If liquid flow back to the hot end was underpredicted, flux toward the hot soil would be underestimated. If solute diffusion flux from hot toward cold soil was overestimated, solute concentration at the hot end would be underestimated.

Fig. 7 shows calculated total benzene concentrations for isothermal and nonisothermal conditions 2 h after injecting the benzene at the soil surface. Nonisothermal benzene transfer exceeded isothermal transfer of benzene because of greater temperature range (21–35°C) and gradients in the nonisothermal columns enhancing the volatilization. Clearly, it is necessary to consider the effect of temperature and temperature gradient on benzene movement to correctly predict benzene redistribution within soil and benzene volatilization from soil.

Fig. 8 shows observed and predicted distribution of benzene for isothermal conditions after 7 days. The measured values were similar to the calculated ones in soil near the top

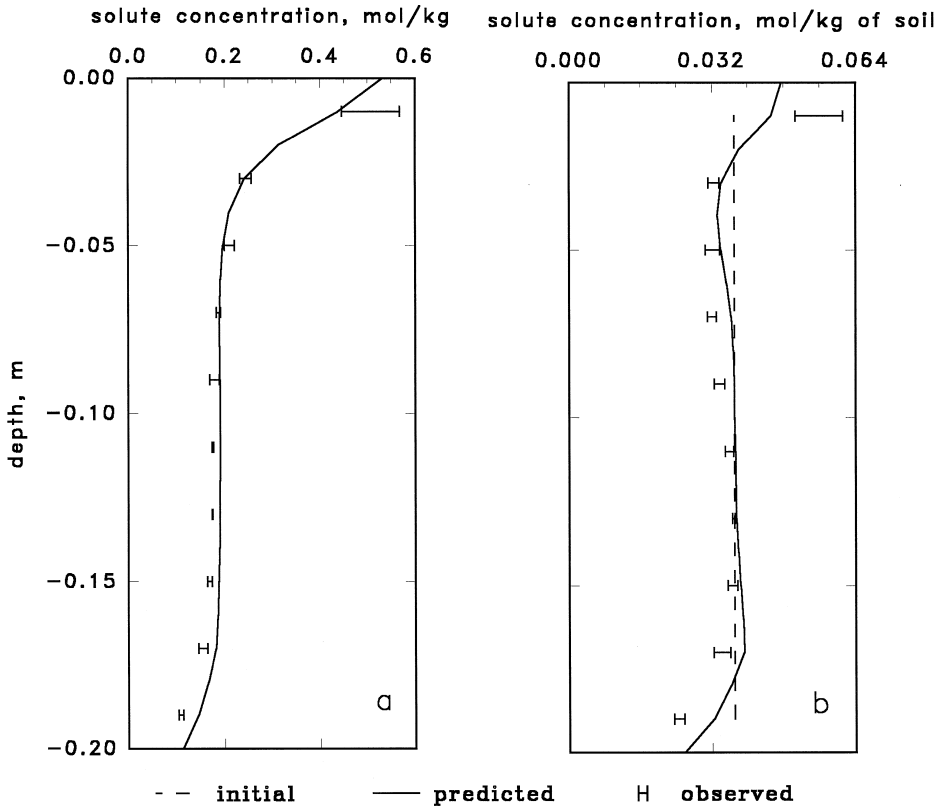


Fig. 6. Measured and predicted solute concentration distributions in soil solution (a) and measured, predicted, and initial solute concentration distributions in soil mass (b).

of soil columns. In the lower half of soil columns, however, the observed values deviated from predicted values. The model predicted that benzene should be evenly distributed along the soil column. Similar deviations from simulated data were observed in other studies. For example, Voudrias and Li, [5] studied benzene concentration distribution numerically and experimentally under isothermal conditions. Their model, based on the movement of benzene by diffusion in the vapor phase and on the assumption of local chemical equilibrium among the three phases of benzene in soil, described the distribution of benzene in dry soil ( $0.001 \text{ m}^3/\text{m}^3$ ) well, but it deviated from the observed values in wet soil ( $0.124 \text{ m}^3/\text{m}^3$ ). They attributed this deviation in wet soil to benzene biodegradation. In our study, biodegradation did not occur because the soil was sterilized. The observed deviation here could have been due to both the experimental error in measuring gas phase benzene concentration or to local soil heterogeneity. The measured values of benzene in the present study showed a peak for the benzene at position 0.12-m depth. Less than predicted concentrations at the bottom of each soil column were observed. The amount of benzene by volume in the soil phases follow the order: liquid > solid > gas.

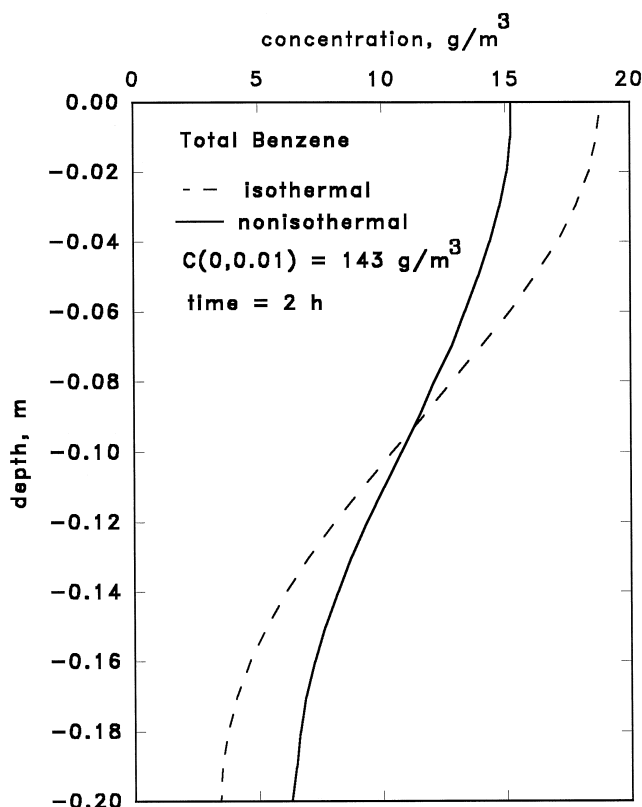


Fig. 7. Predicted total benzene concentration distributions 2 h after application of benzene to the soil surface under isothermal (29°C) and nonisothermal conditions (21 to 35°C).

The predicted and observed benzene distributions in nonisothermal soil columns are presented in Fig. 9. The gas phase concentrations were greatest at the hot end of the soil column, where benzene volatility was the greatest, and water content was the least. Although the solubility of benzene in water was constant for the temperature range studied [14], its volatility decreases by approximately 30% when moving from the hot to the cold end of the soil column (Fig. 3). Consequently, the extent of benzene volatility at the cold end of the soil column was the least and benzene concentration in water the greatest. The observed benzene concentrations in the gas phase matched the model predictions reasonably well, with exception of the positions just below the middle of the column. Interestingly, the water content at those depths was greater than the predicted as well (Fig. 5). The solid phase concentrations were estimated from the calculated values of benzene in the liquid phase and the  $K_{s1}$  value. The total concentration distribution shows less concentration at the hot soil end than at the cold soil end. Both observations and predictions indicated that more benzene moved toward the bottom end of a soil column (cold end) under nonisothermal conditions than under isothermal conditions (Fig. 8). Similar numerical results were reported by Cohen and Ryan [6] under diurnal

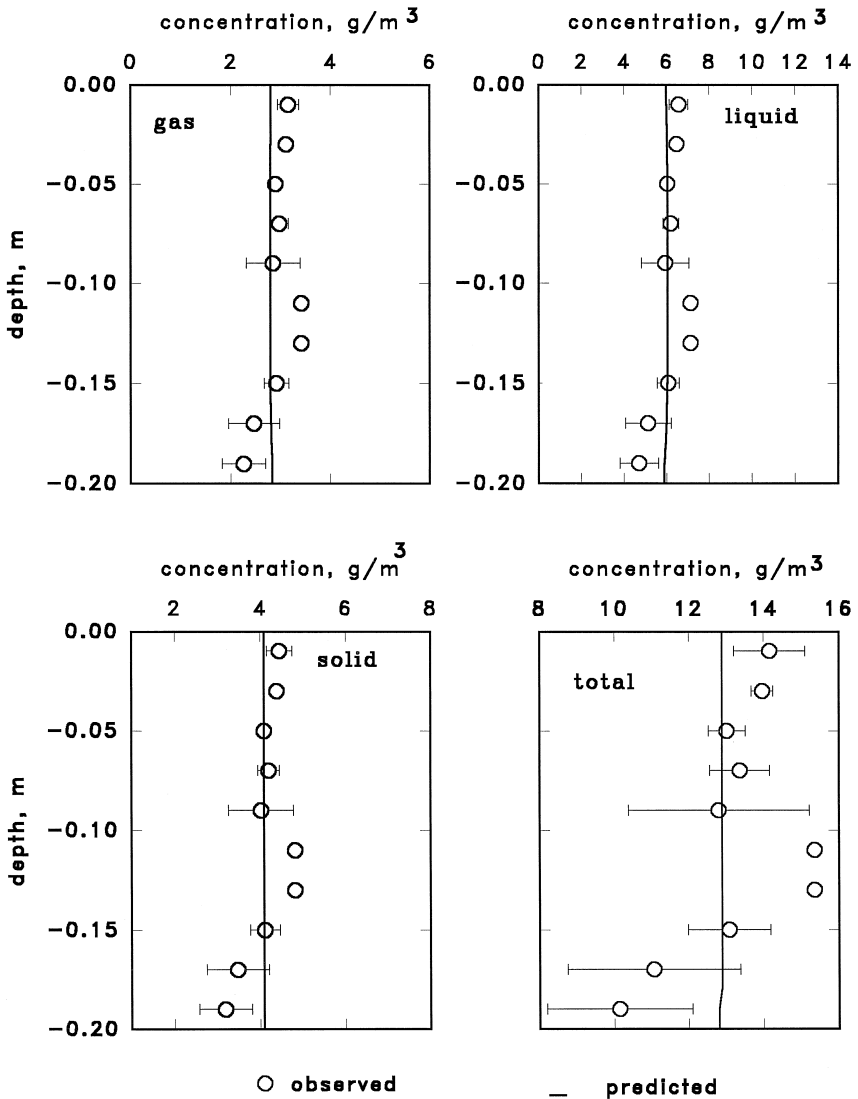


Fig. 8. Measured and predicted benzene distribution under isothermal soil condition.

soil temperature. They reported that benzene volatilization varied diurnally by at most a factor of two, and that this occurred in the absence of water convection.

The distribution coefficient ( $K_{s1}$ ) of benzene is small ( $0.343 \times 10^{-3} \text{ m}^3/\text{kg}$ ). Thus, approximately 65% of the benzene was present in the form of liquid and gas phases. Because Henry's law constant of benzene is high, volatilization of benzene from the liquid phase seems to be a major pathway of benzene transport in the moist unsaturated soil. This is contrary to the very dry soils ( $< 4$  molecular layers of water), where the  $K_{sg}$  values are large (Fig. 2). Thus, benzene volatilization can be relatively small. It has

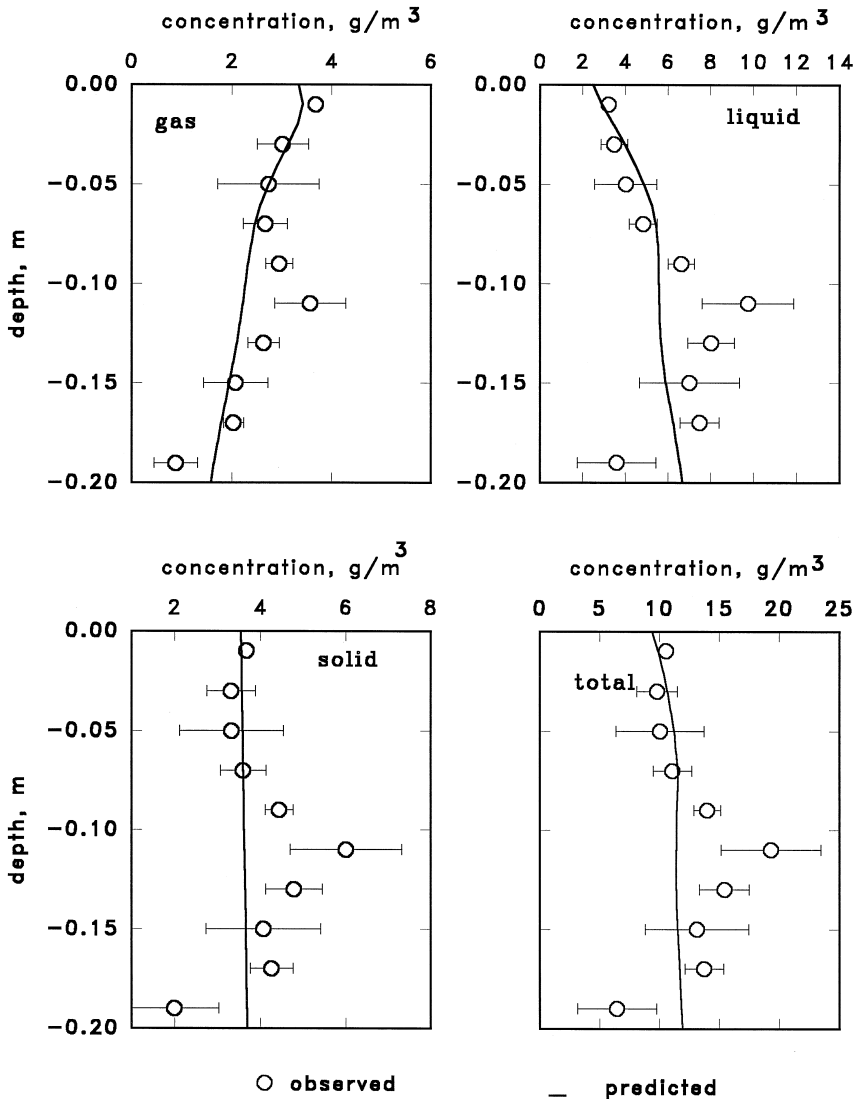


Fig. 9. Measured and predicted benzene distributions under nonisothermal soil condition.

been shown that the presence of a dry soil layer at the surface of landfills can limit the emission of benzene to the atmosphere [4].

Table 1 shows the mean error (ME) and root mean square error (RMSE) for the predicted temperature, water content, chloride concentration, and benzene concentration in the gas phase (Figs. 4–6, 8 and 9). The ME value was 0.12°C for predicted temperature. The RMSE value was 0.20°C for the predicted temperature (Fig. 4). The ME of the predicted water content was 0.0001 m<sup>3</sup>/m<sup>3</sup>. The RMSE for the predicted water content was 0.014 m<sup>3</sup>/m<sup>3</sup> (Fig. 5). The ME value of the predicted chloride

Table 1

The calculated mean error (ME) and root mean square error (RMSE) for the data presented in Figs. 4–6, 8 and 9

ME or RMSE	4	5	6	8	9 <sup>a</sup>
ME	0.1180	0.0001	−0.0019	−0.1467	−0.2419
RMSE	0.2026	0.0143	0.0460	0.3870	0.5698

<sup>a</sup>These numbers are the numbers of the figures.

concentration was  $-0.0019$  mol/kg, and the RMSE was  $0.046$  mol/kg (Fig. 6). The ME of predicted benzene concentration in the gas phase under isothermal condition was  $-0.15$  g/m<sup>3</sup>, and the RMSE was  $0.387$  g/m<sup>3</sup> (Fig. 8). The ME and RMSE of predicted benzene concentration in the gas phase under nonisothermal condition (Fig. 9) were  $-0.24$  and  $0.57$  g/m<sup>3</sup>, respectively. It can be concluded that the model described the mechanisms of water, heat and chloride flows well under the conditions of the present study. The model was also appropriate for the prediction of benzene redistribution under isothermal and nonisothermal conditions.

#### 4. Summary and conclusions

Isothermal and nonisothermal heat and mass transfer was studied experimentally by using closed soil columns. Benzene as an organic volatile chemical and KCl as an inorganic chemical were added to unsaturated soil. A theory of heat and mass transfer was used to predict temperature, water content, benzene concentration and KCl concentration within the soil columns. The predicted soil temperature was in agreement with the observed temperature. The predicted and observed water content distributions were in agreement. The net water transfer to the cold region of soil columns was slightly underpredicted. The underprediction of water was the result of the underestimation of the water vapor transfer or overestimation of liquid water transfer. Chloride redistributed along the nonisothermal soil columns, and it accumulated in the hot surface region of soil columns. The predicted and observed benzene distributions were similar except at positions of 0.12 to 0.14 m where the measured gas phase concentration was greater than predicted. This study showed that soil temperature and temperature gradients are important for correctly predicting benzene transport within soil, and benzene volatilization from soil. The application of this theory may be very useful for the development of remediation strategies to clean soil from volatile compounds when nonisothermal conditions exist. It should also be useful for monitoring VOC redistribution at contaminated sites.

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