

Moisture effect on the transport of organic vapors in sand

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Abstract

Vapor-phase affects the transport, lifetime, and fate of volatile organic contaminants in soils. Furthermore, it has an effect on the assessment and the selection of a remediation approach. The diffusion of dichloromethane (DCM), 1,1,1-trichloroethane (TCE) and carbon tetrachloride (CTC) in dry and wet sand media were investigated using a packed column at room temperature. The apparent diffusion coefficients, D_{app} , which accounts for effective diffusion and sorption of DCM, TCE and CTC were determined by fitting the experimental data to a diffusion model. The apparent diffusion coefficients of DCM, TCE and CTC for wet sand were found to be larger than the corresponding values for dry sand. The presence of water reduced retardation factors expressed in terms of the sorption capacity for each compound. The results indicated that dry mineral surface provided dominant sorption sites. This is reflected in greater amounts of organic vapors adsorbed under dry conditions. On the other hand, lower sorption capacities for organic compounds on vapor–water interface than on vapor–mineral interface and their low solubilities resulted in smaller retardation factors in wet sand. The experiments clearly demonstrate the role of humidity in sorption and transport of vapors in sand. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Volatile organic compounds (VOCs) can be introduced into the subsurface environment from a number of sources. These include accidental spills on the soil surface, leaking from underground storage tanks, and disposal facilities [1–3]. Vapor-phase diffusion is an important transport mechanism for many contaminants such as VOCs in unsaturated soils. Vapor-phase diffusion affects the transport and fate of these contaminants in soils. Furthermore, it has an effect on the assessment and the selection of a remediation approach.

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Many factors influence the transport and diffusion of VOCs in soils. More research is needed to understand fully the effects of environmental conditions, VOC and soil properties, and sorption characteristics.

The most common approach in modeling diffusion and sorption of VOC in soils is to use a model with a single parameter, the apparent diffusivity, D_{app} . D_{app} accounts for retardation of diffusive transport by sorption as well as the effects of tortuous paths that molecules are required to take through the porous media. Previous studies have been reported that the apparent diffusivities of VOCs in soils depend on soil properties, temperature, and soil moisture [4,5]. Sorption type (linear equilibrium, non-linear BET isotherm, etc.) can also affect the apparent diffusivity in soils. Shonnard et al. [2] evaluated the effects of non-linear BET sorption on the atmospheric emission rates of benzene and dichloromethane from soils measured in a one-dimensional soil column under unsteady-state conditions. They concluded that when a diffusion model was used to interpret emission rate data from diffusion experiments in which non-linear sorption occurred, apparent diffusivities varied with initial VOC concentration in the soil.

The results of several experimental studies showed that retardation factors which depend on the sorptive capacity of the soil will vary considerably depending on the nature of the contaminants, and the composition and moisture content of the soil. Vaudrias and Li [6] and Li and Vaudrias [1] evaluated the effects of vapor-phase adsorption, soil moisture, and soil organic carbon on the migration of benzene, jet-fuel cycloalkene, and some other aromatic vapors in unsaturated soil. They concluded that retardation values increased with decreasing water content of the soil. Batterman et al. [7] measured retardation and diffusion coefficients for hydrocarbon vapors in unsaturated soils. Their results for methane showed no effects of humidity and soil type on retardation factors. However, toluene and trichloroethylene were retarded by low-humidity media. More recently, Kim et al. [8] investigated the transport of organic chemicals in a water-unsaturated porous medium using laboratory columns. They observed a consistent trend of increasing retardation with decreasing water content, and concluded that air–water interfacial adsorption was a significant factor for the retardation of *n*-alcohols. Many model studies for describing VOC transport in the soil environment have been also reported in the literature. Roy and Griffin [9] analyzed theoretically the interaction and static movement of 37 organic solvents as vapors through the unsaturated soil zone. Baehr [10] discussed the use of analytical solution for the diffusion equation with retardation. Cabbar and McCoy [11] examined the effect of sorption process on the diffusion of VOCs in moist soil. Using temporal and volume averaging methods, mathematical expressions were developed and evaluated for soils consisting of porous and non-porous particles.

The objective of the current study was to determine the apparent diffusion coefficients, the retardation factors, and the sorption coefficients of dichloromethane (DCM), 1,1,1-trichloroethane (TCE) and carbon tetrachloride (CTC) on dry and wet sand using laboratory columns under unsteady-state conditions.

2. Materials and method

Experiments were carried out with DCM (Merck), TCE (Merck) and CTC (Merck) using packed column under unsteady-state conditions. All chemicals were of at least 99% purity. Sand from the surface reserves in Kazan region near Ankara was used as the adsorbent. The

Table 1
Chemical composition of the sand (wt.%)

SiO ₂	68.08
TiO ₂	0.25
Na ₂ O	3.30
Al ₂ O ₃	14.65
CaO	5.90
K ₂ O	2.30
Fe ₂ O ₃	3.93
MgO	1.40
Loss on ignition	0.27

sand was air-dried, passed through a 0.4 mm sieve, and mixed thoroughly to obtain a homogeneous mixture. The specific surface area of the sand was measured by low-temperature nitrogen adsorption as well as by mercury intrusion technique [12]. The nitrogen adsorption and mercury intrusion tests were carried out in a Quantachrome Monosorb apparatus and Quantachrome 60 Mercury porosimeter, respectively. Surface area obtained from mercury intrusion technique (8.3 m²/g sand) was almost the same as the value obtained from nitrogen adsorption (8.4 m²/g sand). These results indicated that the sand did not have micropores. The mercury intrusion result was also interpreted to obtain grain porosity (0.12) and pore-size distribution. The grain density was found as 2.6 g/cm³ using helium pycnometer (Micromeritics Multivolume Pycnometer 1305). Chemical composition of the sand sample (Table 1) was determined with the use of the International Standard, ISO 10058 [13]. Elemental analysis of organic matter and total sulfur were determined using Leco total sulfur and carbon–hydrogen–nitrogen analyzer (Table 1). In this instrument, the organic fraction is burned and gaseous effluents are analyzed. The loss on ignition value (0.27 wt.%) was 0.07% C, 0.05% N, 0.07% S, and 0.08% H.

Oven-dried sand and sand with a moisture content of 0.06 g water/g sand were used to determine the transport behavior of DCM, TCE and CTC. Dry sand was prepared by heating a sample in an oven at 110°C until it came to constant weight. Wet sand was prepared by thoroughly mixing appropriate amounts of sand and water. Water uptake of the sand was also determined from the weight change at different relative humidities. A water uptake of 0.06 g water/g sand was observed at 90% relative humidity.

A glass column with an inside diameter of 5 cm and a length of 70 cm was used for the experiments (Fig. 1). Thin porous glass disks were used at each end of the column to support the sand. The length of the column packed with sand was 64 cm. To minimize soil stratification, a careful and successive packing process was followed, i.e. by filling the column with sand and then compacting it using a long wooden rod in a stepwise manner. After column was packed with sand, bulk density and void porosity were determined using the following equations.

$$\rho_b = \frac{W}{V} \quad (1)$$

$$\varepsilon_T = \frac{1 - \rho_b}{\rho_p} \quad (2)$$

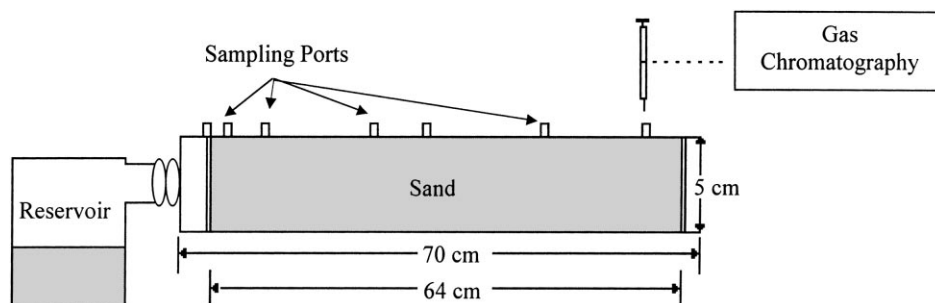


Fig. 1. A schematic diagram of packed column used in these studies.

$$\varepsilon_w = \frac{M\rho_b}{\rho_w} \quad (3)$$

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

where ρ_b , ρ_p and ρ_w are the bulk density on dry weight basis, the particle density and water density in g/cm^3 at 20°C , respectively, W is the mass of oven-dried sand used for packing the column (g), M is the moisture content (g water/g sand), V is the total volume (cm^3), and ε_T , ε_w , and ε_a are the total porosity, the water-filled porosity and the air-filled porosity, respectively. The ε_w was zero for the column when packed with the dry sand.

The inlet of glass column was connected to a reservoir (2000 ml volumetric flask) containing 1000 ml of DCM, TCE or CTC. The column was equipped with seven sampling ports located along the column axis at distances, z , of 0, 0.5, 3.9, 24.3, 39.0, 51.3, and 61.3 cm from the inlet (Fig. 1). These ports were not uniformly distributed on the column. Each sampling port was fitted with a gastight cylindrical septum. All experiments were conducted at room temperature. To establish a steady-state vapor concentration in the first port the reservoir was first connected to an empty column for a period of 72 h before starting each experiment. During the 72 h period, vapor samples collected from the first port were analyzed to confirm that the measured vapor concentrations reached the steady values and remained constant. The reservoir was then connected to the column packed with sand, and the measurement time was started.

DCM, TCE or CTC vapor samples of 0.1 ml in volume were collected with a gastight syringe. All vapor samples collected from the sample ports were periodically analyzed by a GC (Gow Mac Series 350). The GC was equipped with a Chromosorb-P column and TCD, and was operated under isothermal conditions at 90°C . Injection port and detector temperatures were 115 and 110°C , respectively. Different volumes of the liquid sample for DCM, TCE and CTC were placed in 50 ml glass vials. These glass vials were placed at 80°C for several hours to allow the complete vaporization of all liquid. Standard vapor obtained in this way were taken from headspace of the vials and analyzed by GC. These analyses demonstrated that a linear relationship between vapor concentration and detector response (peak area) as expected. Quality assurance checks were made before starting and finishing daily runs using DCM, TCE or CTC standards, and showed relative errors of 1–3%.

There was no measurable pressure gradient along the sand column when measured with a water-filled inclined manometer. Radial dispersion was neglected based on the results of preliminary tests made by collecting samples at different radial positions, which showed identical concentration value.

3. Theory of vapor-phase diffusion in packed column

The essential fundamental step in describing packed-bed non-connective transport mathematically is to establish the governing diffusion equation, and the appropriate initial and boundary conditions. The one-dimensional conservation equation of mass with no chemical reaction for DCM, TCE and CTC in isotropic and homogeneous unsaturated sand yields the following diffusion equation.

$$\frac{\partial C}{\partial t} = D_{\text{app}} \frac{\partial^2 C}{\partial z^2} \quad (5)$$

where C is DCM, TCE or CTC concentration in pore air (g/cm^3), D_{app} is the apparent diffusion coefficient, z is the distance coordinate, and t is the time. Using the local equilibrium assumption to describe vapor distribution between water-, air- and soil-phases, D_{app} can be expressed by the following equation [1,10,11].

$$D_{\text{app}} = \frac{D_{\text{we}}/K_{\text{H}} + D_{\text{eff}}}{\varepsilon_{\text{a}} R} \quad (6)$$

where D_{eff} is the effective diffusion coefficient of DCM, TCE or CTC for air-filled porosity, D_{we} is the effective diffusion coefficient in water existing in the porous medium, K_{H} is the air–water partition coefficient (Henry's Law constant), and R is the retardation factor. For dry sand, Eq. (6) reduces to

$$D_{\text{app}} = \frac{D_{\text{eff}}}{\varepsilon_{\text{a}} R} \quad (7)$$

The retardation factor expressed in terms of the sorption capacity is defined as follows [1,10,11]:

$$R = 1 + \frac{\varepsilon_{\text{w}}}{\varepsilon_{\text{a}} K_{\text{H}}} + K_{\text{obs}} \frac{\rho_{\text{b}}}{\varepsilon_{\text{a}}} \quad (8)$$

where K_{obs} is the combined linear sorption coefficient which includes all the partitioning processes. In the presence of water, the organic vapors' sorption might occur by (1) adsorption from the vapor-phase to the mineral surface, (2) dissolution into soil organic carbon, (3) adsorption on the surface of a water film that is adsorbed on the mineral, (4) dissolution into an adsorbed water film, (5) adsorption onto water–mineral interface [14]. With non-porous particles under nearly dry conditions, K_{obs} would predict vapor sorption onto mineral (sand) surfaces and dissolution into soil organic carbon. Under high moisture conditions, however, the water film is probably thick enough to prevent the influence of the mineral on adsorption. In this case, K_{obs} accounts for (2–5) processes as above.

The initial and boundary conditions for the packed column system can be stated as

$$\text{the initial condition : } C(t = 0, z) = 0; \quad (9a)$$

$$\text{the boundary conditions : } C(t, z = 0) = C_0; \text{ and} \quad (9b)$$

$$C(t, z = L) = 0. \quad (9c)$$

The solution to Eq. (5) with these initial and boundary conditions for a concentration ratio as a function of time and distance is given by Eq. (10) [15].

$$\frac{C}{C_0} = 1 - \frac{z}{L} - \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin\left(\frac{n\pi z}{L}\right) \exp\left(\frac{-D_{app} n^2 \pi^2 t}{L^2}\right) \quad (10)$$

where L is the column length.

Eq. (10) was used together with the experimental concentration data, obtained at different times and locations, to determine the best-fit values of D_{app} . The steepest-descent method to have a minimum sum of squares of the non-linear model was employed in this analysis [16].

4. Results and discussion

As outlined in Section 3 above, the experimental findings were interpreted with the assumption that the only mechanism of the overall transport of the organic species inside the column was diffusion. Peak areas measured for the vapor concentration at every sampling port divided by the peak area detected for the vapor concentration of the corresponding compound for the same run in the first sampling port was equal to the vapor concentration ratio, C/C_0 . These concentration ratios plotted as a function of time for DCM (Fig. 2) for dry and wet sand columns. Similar curves were obtained for TCE and CTC. These experimental concentration profiles for DCM, TCE and CTC with respect to time and distance were analyzed using Eq. (10) for dry and wet sand columns. The solid lines in figures (Fig. 2) are the best-fit curves of Eq. (10), superimposed on the experimental data points. The good agreement between Eq. (10) and experimental data suggested that the diffusion equation was an adequate model in describing DCM, TCE and CTC vapor diffusion in both dry and wet sand. The concentration at steady-state conditions decreased linearly along the column length for each tracer in both dry and wet sand columns (Fig. 3). Using the same initial and boundary conditions (Eq. (9)), the solution of Eq. (5) at steady-state becomes

$$\frac{C}{C_0} = 1 - \frac{z}{L} \quad (11)$$

Some of the experimental data deviate from the model values calculated using Eq. (11) (solid lines in Fig. 3). This difference may be due to the experimental error and slight heterogeneities within the system.

The apparent diffusion coefficients for each compound, D_{app} , determined by fitting Eq. (10) to the experimental data are tabulated in Table 2. The apparent diffusivity of

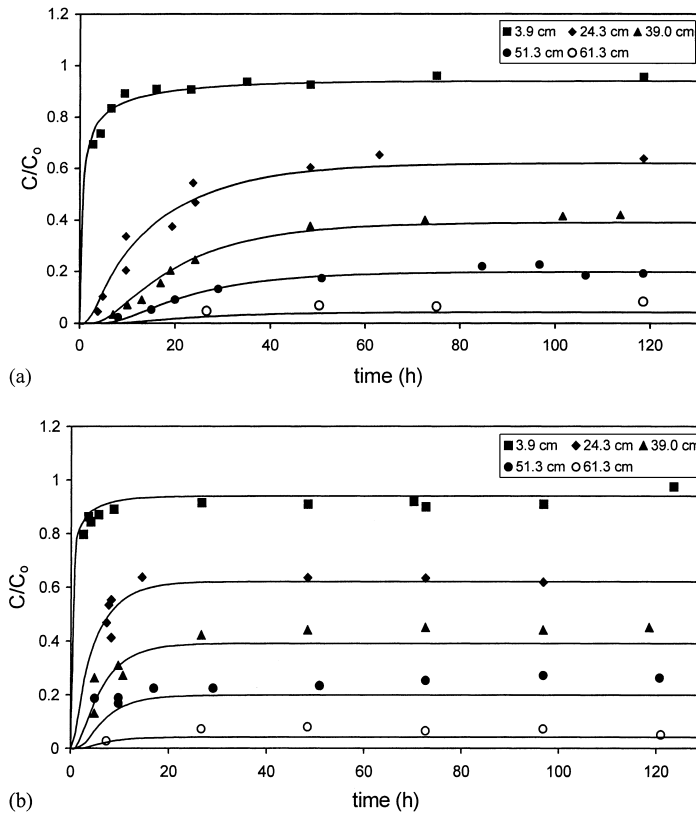


Fig. 2. Experimental and calculated concentration profiles for dichloromethane (DCM) vapor: (a) in dry; (b) in wet sand column.

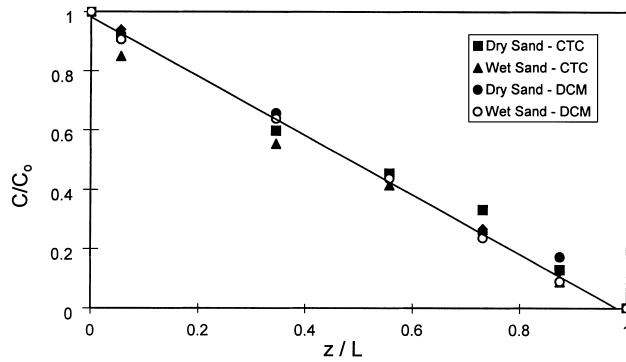


Fig. 3. Steady-state concentration profiles of dichloromethane (DCM) and carbon tetrachloride (CTC) vapors vs. dimensionless distance (z/L) for dry and wet sand.

Table 2

The apparent diffusion coefficient (D_{app}), retardation (R), and sorption parameters ($\rho_b K_{obs}$) for dichloromethane (DCM), 1,1,1-trichloroethane (TCE) and carbon tetrachloride (CTC)

Component	Dry sand			Wet sand		
	D_{app} (cm ² /s)	R	$\rho_b K_{obs}$	D_{app} (cm ² /s)	R	$\rho_b K_{obs}$
CTC	0.0035	17.74	10.91	0.0200	2.63	0.92
TCE	0.0016	58.80	37.57	0.0094	19.42	12.85
DCM	0.0070	11.72	6.70	0.0235	2.81	0.99

DCM reported by Shonnard et al. [2] in air-dry Auberry sand loam with porosity 0.49 was 6.88×10^{-3} cm²/s. In the present work, the apparent diffusivity of DCM in oven-dry sand ($\varepsilon_a = 0.65$) was 7.0×10^{-3} cm²/s which was in close agreement with Shonnard et al. [2]. The apparent diffusion coefficient, D_{app} , included the effect of both sorption and the effective diffusivity. As expected, the apparent diffusivity of DCM, TCE and CTC in wet sand was greater than that of dry sand because of the reduction in vapor-sorption capacity. Under dry conditions, adsorbed concentrations may increase because vapors are directly in contact with the dry mineral surface. The reason for the decreased vapor-sorption capacity in wet sand was the competition between water and volatile organic compound molecules for sites on the mineral surface.

The diffusion coefficient for a gas or vapor in porous media is less than that in free air because of to the relatively obstructed paths for movement of the molecules. The effective diffusion coefficient (porous-media diffusion coefficient) was derived from the application of the Millington-Quirk [17] model from the following equations:

$$\tau_w = \frac{\varepsilon_T^2}{\varepsilon_w} \quad (12)$$

$$\tau_a = \frac{1}{\varepsilon_a^{1/3}} \quad (13)$$

$$D_{we} = D_{wAB} \frac{\varepsilon_w}{\tau_w} \quad (14)$$

$$D_{eff} = D_{AB} \frac{\varepsilon_a}{\tau_a} \quad (15)$$

The molecular diffusion coefficient in free air, D_{AB} , was determined by Chapman-Enskog equation [17]. The molecular diffusion coefficient, D_{wAB} , in bulk water, was calculated from the Wilke-Chang equation [18].

Retardation factors were then calculated for each compound using the fitted values of D_{app} together with D_{eff} and D_{we} (Eq. (6) or (7)). Under the oven-dry conditions, K_{obs} was obtained from Eq. (8) by assigning ε_w as zero. Under dry condition, DCM, TCE or CTC vapors directly interact with the mineral surface and soil organic matter. The sorption coefficient on gas-dry solid surface of TCE and CTC was in fair agreement with data in the literature [19,20]. The lack of stronger agreement may have been the result of the use of

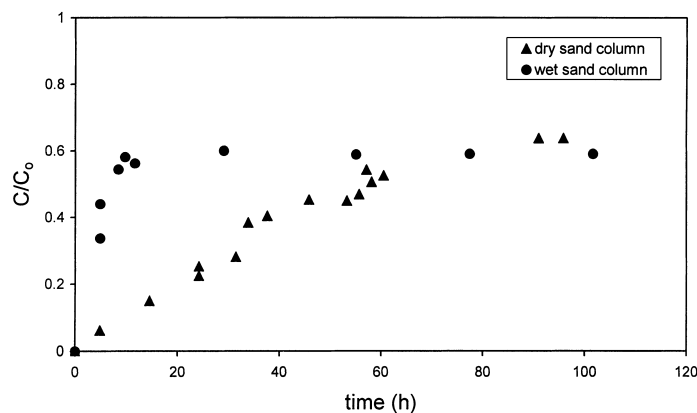


Fig. 4. Experimental concentration profiles for carbon tetrachloride (CTC) vapor taken from third sampling port.

different types of sorbent (sand) in the experiments. At the high moisture content K_{obs} , which includes: (a) dissolution into soil organic carbon; (b) adsorption on the surface of the water film; (c) dissolution into the adsorbed water film; and (d) adsorption onto water–mineral interface effects, was also computed by Eq. (8) for each vapor tracer (Table 2).

The rate of axial transport along the column length was slower in dry sand than wet sand column. Fig. 4 shows explicitly that CTC concentrations at third sampling port reached steady-state value after approximately 100 h for the dry and 20 h for wet sand column. This indicated that the retardation factors for DCM, TCE and CTC for the wet sand column were less than those for dry sand column. However, Li and Voudrias [1] observed that retardation factors of some aromatics (benzene, toluene, ethylbenzene) and some cycloalkanes (cyclohexane, methylcyclohexane) were greater for wet soil than for the dry soil collected from south of Waycross, Georgia with a similar experimental approach. Their explanation about the greater retardation in wet soil was the significant solubility of aromatics and cycloalkanes in water that retarded the rate of transport.

In this study, retardation increased in dried sand, because of adsorption at vapor–mineral interface, which was in agreement with the results reported by other researchers [7,11]. The increased rate of transport and the lower retardation factors in wet sand resulted from low sorption affinities of DCM, TCE and CTC on vapor–water interface, and their low solubilities. The experiments clearly demonstrated the role of humidity as well as the effect of solubility in sorption and transport of vapors in sand. This investigation may be especially germane to applications that involve gas-phase transport processes, e.g. soil gas monitoring and in situ remediation of contaminated soils.

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