Sorption and Diffusion of Chlorinated Methanes in Moist Clay

H. Canan Cabbar and Nesrin Varol
Dept. of Chemical Engineering, Gazi University, Ankara, Turkey 06570

Benjamin J. McCoy
Dept. of Chemical Engineering and Materials Science, University of California, Davis, CA 95616

The dynamic behavior of chlorinated methanes in clays exposed to relative humidities (RH) from 0 to 80% was investigated with the single-pellet pulse-response moment technique. Values of effective diffusion coefficients obtained from zeroth moment analysis differed only slightly for dry and moist clay pellets. When the clay pellet was dry, equilibrium adsorption constants of dichloromethane (D), trichloromethane (T), and carbon tetrachloride (C) at the gas-mineral interface were determined from first moments to be 118, 92, and 90, respectively. Dryness factors (dry fraction of surface area) for clays with RH of 5, 20, 40, and 60% were also calculated from first moments as 0.5, 0.1, 0.04, and 0.01, respectively. When the pore surfaces were covered with the water film (dryness factor was 0 for the pellet at RH 80%), overall equilibrium adsorption constants for the same tracers (D, T, C) at the gas-water and water-mineral interfaces were determined to be 7.5, 7.2, and 3.6, respectively.

Introduction

Adsorption of volatile organic compounds (VOCs) on soil is important in contaminant migration and soil remediation. Since moisture is usually present, an understanding of how VOCs interact with water-soil mixtures is needed. The migration of such pollutants in soil involves both transport and adsorption processes. Transport by diffusion depends on the pore structure of the soil. Adsorption depends on surface area (hence, pore structure), composition, and moisture content. Numerous studies (Rogers et al., 1980; Garbarini and Lion, 1986; Chiou and Shoup, 1985) focused on VOC adsorption in dry soils. Cabbar et al. (1994, 1996) applied the single-pellet moment method to determine diffusion and adsorption parameters for chlorinated ethanes on dry soil, and also the effect of SOM on dichloromethane sorption in a dry simulated soil.

Several authors have considered the effect of moisture on VOC sorption in soil and clay materials. Pennell et al. (1992) examined competitive adsorption of *p*-xylene and water by considering four equilibrium processes for moist soil particles: adsorption at the gas-liquid interface, dissolution into adsorbed water, partitioning into soil organic matter, and adsorption on mineral surfaces. Chiou and coworkers (1985) investigated sorption of organics on soil and attributed the isotherm linearity at high relative humidity (RH) to dissolution in soil organic matter. Thibaud et al. (1993) investigated the effect of moisture on the sorption-desorption of chlorobenzene and toluene using a dynamic technique based on frontal analysis chromatography. Cabbar and McCoy (1996), applying a model similar to McCoy and Rolston (1992), developed an expression for the retardation factor that accounts for the effects of water layers partially covering organic and mineral surfaces. Batterman et al. (1995) found retardation and dispersion coefficients for hydrocarbon vapors using transient methods in unsaturated soils. Goss (1993) investigated VOC sorption on clay minerals and found adsorption at the gas-water interface when RH exceeded the value needed for a monolayer to form on the adsorbent. At low RH, VOC uptake increased due to adsorption on dry mineral surfaces. Unger et al. (1996) developed an equilibrium partitioning model to predict the effect of soil moisture content on vapor-phase sorption.

These articles illustrate that the complex interaction of soil, water, and VOCs is a challenging field of research. A thorough understanding of how moisture affects VOC behavior in soil will require further advances in both experimental and theoretical approaches. In the current work, we employ the pulse-response moment technique, previously used for catalyst pellets (Dogu and Smith, 1975, 1976), to study diffusion and adsorption of chlorinated methanes in single pellets of moist soil.

Materials and Method

The dynamic version of the Wicke-Kallenbach diffusion cell was originally proposed by Dogu and Smith (1975, 1976) for measurement of effective diffusivities and adsorption equilibrium constants in porous catalyst pellets. Later, it was shown that the single-pellet moment technique could be successfully used to evaluate tortuosity factors (Wang and Smith, 1983), reaction rate parameters, and permeability of porous solids (Dogu et al., 1986, 1989). More recently, the technique was adopted for characterization of VOC sorption and diffusion in dry soil (Cabbar et al., 1994, 1996). To determine the effect of soil organic matter on VOC sorption, Cabbar et al. (1996) determined the dynamic behavior of dichloromethane for several humic acid loadings on a single pellet of natural clay.

In the single-pellet moment technique, a cylindrical clay pellet with known physical properties and chemical composition is prepared by pressing the clay into a ring-shaped stainless-steel holder. The origin, composition, and preparation of the current clay samples were identical to those described in Dogu et al. (1996). Likewise, the apparatus and flow rates, and therefore the mass transfer and mixing conditions, were the same, as was the detection method (TCD), in these experiments and in Cabbar et al. (1996). The single-pellet cell is placed in the oven of the gas chromatograph (Varian Vista 6000). Except for the addition of a water-saturation system shown in Figure 1, the apparatus is similar to that described in previous studies (Dogu and Smith, 1975).

Carrier gas (helium) with the desired relative humidity was passed over both faces of the clay pellet. Adjustment of relative humidity was achieved by splitting the gas stream from the helium cylinder into two secondary streams and diverting one to a water saturator. The water concentration in the carrier gas streams was determined by magnesium perchlorate traps (Figure 1). The difference between initial and final trap weights yielded total mass of vapor in the gas stream. Convective transport through the clay pellet was eliminated by adjusting the pressures at the pellet ends to be equal. A 1.00 μL pulse containing the adsorbing or diffusing component was introduced into the stream flowing over the upper face of the pellet, and the response peak was measured with the thermal-conductivity detector placed in the stream leaving the lower face. Time delay of the response curve depends on effective diffusivity and adsorption equilibrium constants for the tracer (D, T, or C) in the clay pellet. These experiments were conducted at several lower-face-stream flow rates and at 30°C. Material balances on initial experiments for testing the adsorption reversibility of D, T, and C showed that adsorption was reversible. We used a small tracer amount (1.00 μL pulse) to ensure adsorption linearity, which was confirmed with different-sized pulses.

Theory

The differential mass balance for transport of diffusing component (dichloromethane, trichloromethane, or carbon tetrachloride) within the moist clay pellet can be expressed as (Cabbar and McCoy, 1996)

$$\epsilon_p \frac{\partial C_A}{\partial t} = D_e \frac{\partial^2 C_A}{\partial x^2} - \rho_p \left[dK_{gm} + (1-d)\left(\frac{K_{lm}}{K_H} + K_{gl} \right) \right] \frac{\partial C_A}{\partial t} \tag{1}$$

where we consider adsorption at gas-mineral, liquid-mineral, and gas-liquid surfaces. Here, D_e is pellet-effective diffusiv-

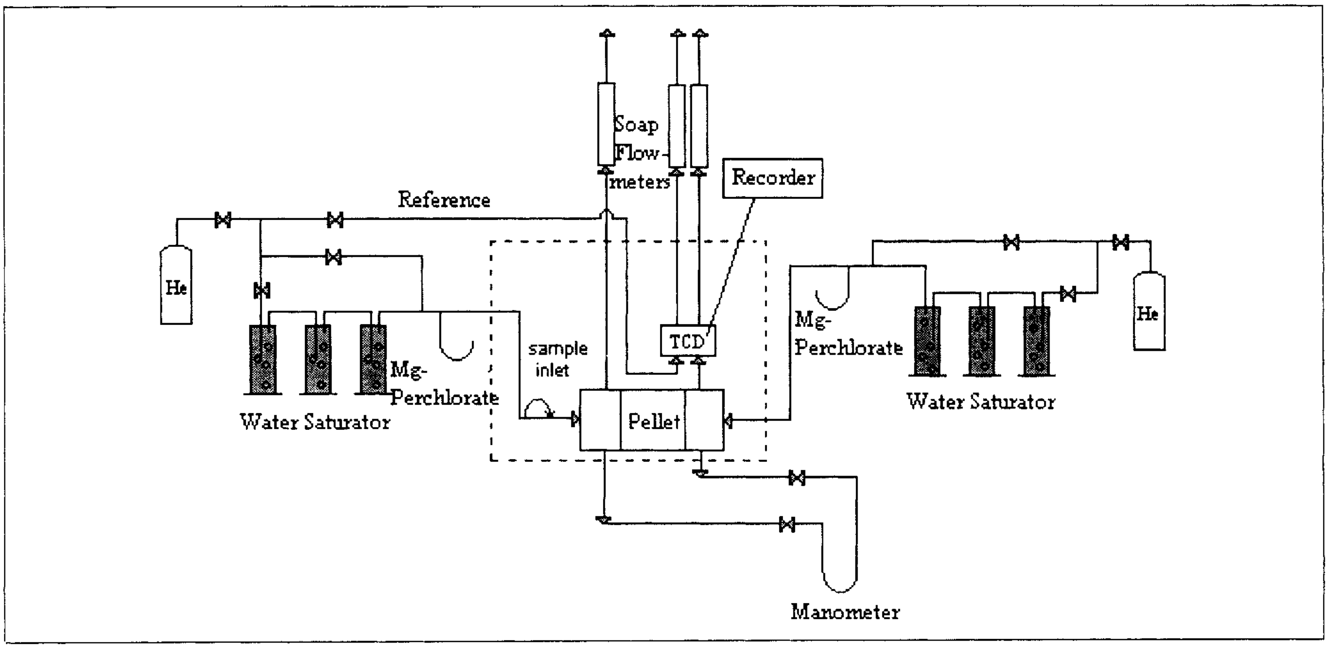

Figure 1. Experimental apparatus with water saturator.

ity, ϵ_p is total porosity of the pellet, ρ_p is pellet density, d is the dryness factor (dry fraction of surface area), K_H is the solubility constant, and K_{gl}, K_{gm}, and K_{lm} are adsorption equilibrium constants. Subscripts g, l, and m refer to gas, liquid, and mineral, respectively. At low relative humidity, the clay surface will not be completely covered with water (Cabbar and McCoy, 1996; Goss, 1993). If the water film is assumed uniform in thickness, then the fraction of wetted pore surface is $(1-d)$. Chlorinated methane can be adsorbed on the dry fraction of the mineral surface d or on the fraction $1-d$ covered by liquid.

Because adsorption linearity can be assumed for small tracer concentrations, a moment analysis can easily be performed (Dogu and Smith, 1975, 1976). The initial condition is $C_A(x, t=0)=0$. After Laplace transformation of the partial differential equation (Eq. 1) and boundary conditions at $x=0$ [where $C_A = M\delta(t)$] and at $x=L$ [where $-AD_e(\partial C_A/\partial x) = FC_A$], the resulting ordinary differential equation is solved. Theoretical moment expressions are obtained for the nth moment by applying derivative and limit operations

$$m_n = \int_0^\infty C_A(L,t)t^n dt = (-1)^n \lim_{s\to 0} \frac{d^n(\bar{C}_A)_{x=L}}{ds^n} \tag{2}$$

Dogu and Smith (1975, 1976) discussed details of the boundary conditions and assumptions.

The zeroth moment expression for the tracer is

$$m_0 = \frac{M}{1+\dfrac{L}{AD_e}F} \tag{3}$$

which is independent of moisture content, and, thus, identical to Cabbar et al. (1994, 1996). Here, A is the end-face area of the pellet, L is the pellet length, F is the lower-face stream volumetric flow rate, and M is the input-pulse strength. The first moment (retention time) is

$$\mu_1 = \frac{m_1}{m_0} = \frac{L^2\left(3\dfrac{A}{L}D_e+F\right)}{6D_e\left(\dfrac{A}{L}D_e+F\right)}\left\{\epsilon_p + \rho_p\left[dK_{gm} + (1-d)\left(K_{gl}+\frac{K_{lm}}{K_H}\right)\right]\right\}. \tag{4}$$

which reduces to the Cabbar et al. (1996) expression when $d=1$.

Results and Discussion

Rearranging Eq. 3 gives a linear relation between the inverse of the zeroth moment and the flow rate of the lower-face carrier-gas stream,

$$\frac{M}{m_0} = 1 + \frac{L}{AD_e}F \tag{5}$$

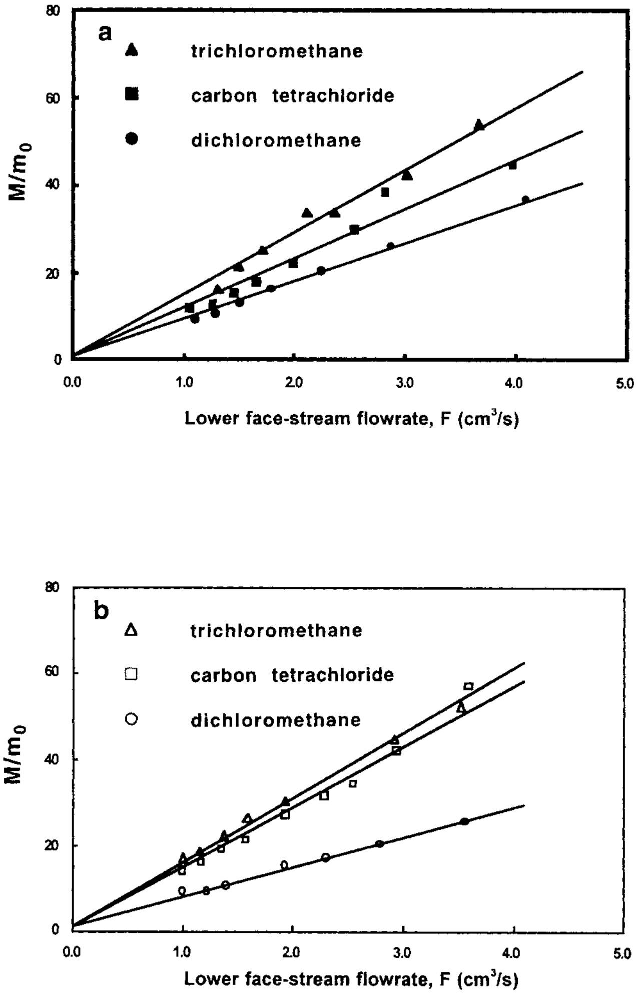

Figure 2. Zeroth moment data for *D*, *T*, *C*: (a) at 0% RH; (b) at 80% RH.

Experimental values of moments (Eq. 2) for D, T, and C were obtained by numerical integration of response data at the outlet of the lower-face carrier-gas stream. From slopes of linear plots of M/m_0 vs. F with an intercept of unity (Figure 2), effective diffusivities were evaluated and results tabulated in Table 1. The effective diffusivities of chlorinated methane (D, T, C) varied only slightly (within experimental error) with moisture content. The effective diffusion coefficient is, however, a strong function of pore structure. For several dry simulated soils with porosity 0.42–0.45, the dichloromethane effective diffusivity reported by Cabbar et al. (1996) was 0.023 ± 0.001 cm^2/s. In the present work, the dichloromethane effective diffusivity was 0.024 cm^2/s for

Table 1. Diffusion and Sorption Parameters of Different Chlorinated Methanes in Clay

Tracer	D_e (cm^2/s) (0% RH)	D_e (cm^2/s) (80% RH)	$\rho_p K_{gm}$ (0% RH)	$\rho_p K'$ (80% RH)
Dichloromethane	0.024	0.030	118	7.5
Trichloromethane	0.015	0.014	92	7.2
Carbon tetrachloride	0.019	0.016	90	3.6

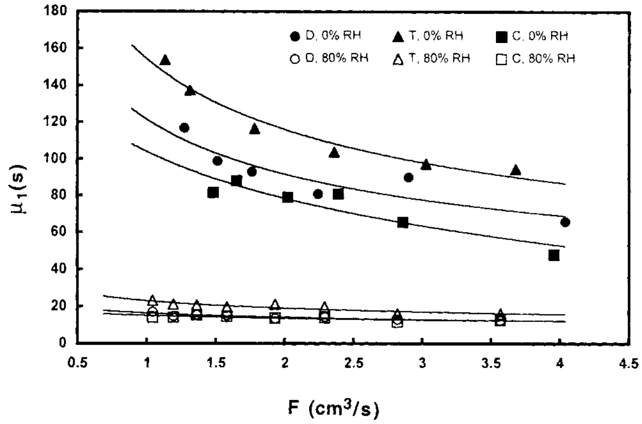

Figure 3. First absolute moment values vs. lower-face stream flow rates.

porosity 0.49. These results agree with each other because of similar pore structure and the relatively small effect of moisture.

The adsorption equilibrium constants, $\rho_p K_{gm}$, of D, T and C at the gas-mineral interface were evaluated from first moment data determined at 0% RH (Figure 3) with dryness factor $d = 1$. Overall adsorption equilibrium constants $\rho_p K' = \rho_p K_{gl} + \rho_p K_{lm}/K_H$ of the same tracers (D, T, C) at the gas-liquid and liquid-mineral interfaces were determined from first moment data (Figure 3) when pores were totally filled with water and $d = 0$ for the pellet at 80% relative humidity. The results obtained by regression analysis for each chlorinated methane at 0% and 80% RH are given in Table 1. Based on effective diffusivities from zeroth moment analysis, the adsorption equilibrium constants at the gas-mineral interface $\rho_p K_{gm}$, the overall adsorption equilibrium constants at the gas-liquid and liquid-mineral interfaces $\rho_p K'$, and the dryness factors d for clays at RH of 5, 20, 40, and 60% were calculated by Eq. 4 and reported in Figure 4.

Measurement of dry surface areas of the pellet for different relative humidities from 0% to 80% was attempted with a Quantachrome Monosorb Sorptometer. A pressed cylindrical clay pellet with known physical properties was saturated with carrier gas at the desired RH. The moist clay pellet was placed into a sorptometer cell. While gas containing 70% He and 30% N_2 passed into the clay pellet, the cell was placed into liquid nitrogen to adsorb N_2 and then automatically removed. Nitrogen is desorbed when the apparatus blows hot air to the cell. For dryness factor determination from surface area data, adsorption of nitrogen on wet and dry surfaces of the soil was assumed. The surface area obtained from the sorptometer can be expressed as a function of dryness factor d.

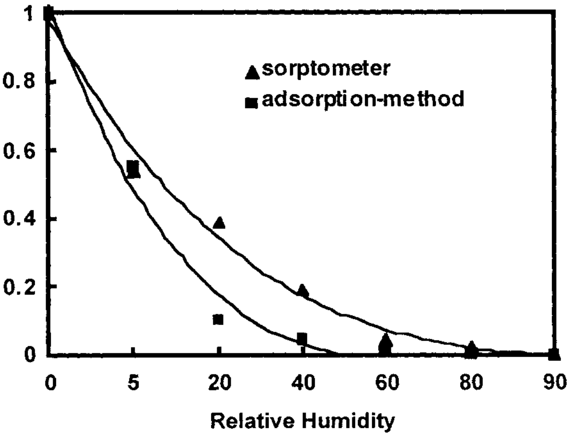

Figure 4. Dryness factors vs. RH measured by pulse response of adsorbate and sorptometer.

Table 2. Clay Pellet Surface Areas and Dryness Factors at Different RHs Determined by Sorptometer Method

RH	S, m^2/g	d_{sorp}
0	40.6	1.000
5	32.1	0.540
20	29.4	0.390
40	25.7	0.190
60	22.9	0.045
80	22.4	0.019
90	22.0	0.000

$$S = dS|_{0\%\ \text{RH}} + (1-d)S|_{90\%\ \text{RH}} \qquad (6)$$

Here, S is greatest when all surface sites are available for nitrogen adsorption (at 0% RH, $d = 1$). As moisture is introduced into the clay, water covers more mineral surfaces and less surface area is available for nitrogen adsorption (Table 2). Dryness factors obtained by the two different methods (pulse-response and sorptometer) are not in exact agreement but follow the same trend as shown in Figure 4. Because the sorptometer measures N_2 adsorption for soil pores filled with frozen water, we should expect only semiquantitative agreement with the 30°C adsorption measurement of d.

Adsorption equilibrium constants for D, T, and C at the gas-mineral interface (Table 1) are different from each other because of differences of dipole moments. The net dipole moments of D, T, and C are 1.8, 1.1, and 0.0 debye, respectively (Reid et al., 1987). The more polar VOCs adsorb more strongly (Cabbar et al., 1994; Batterman et al., 1995; Chiou and Shoup, 1985), in agreement with Table 1. The trend of overall adsorption equilibrium constants $\rho_p K'$ (Table 1) can similarly be explained (Goss, 1992, 1993), since polar substances more easily form hydrogen bonds in the water film. The relatively large value of K_{gm}, however, implies that sorption of D, T, and C on clay is mainly at the gas-mineral interface. The results of this study suggest that evaluation of adsorption equilibrium and effective diffusion coefficients of organic pollutants, as well as dryness factors for the clay pellet, is straightforward with the single-pellet, pulse-response technique.

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