Single-Pellet Dynamics for the Soil Organic Matter Effect on Dichloromethane Sorption

Canan Cabbar and Gülşen Doğu
Dept. of Chemical Engineering, Gazi University, Ankara, Turkey
Timur Doğu
Dept. of Chemical Engineering, Middle East Technical University, 06531 Ankara, Turkey
Ben J. McCoy
Dept. of Chemical Engineering and Materials Science, University of California, Davis, CA 95616

The migration of volatile organic compounds (VOCs) in soil is strongly influenced by soil composition, for example, amount and type of clay, organic matter, and moisture (Chiou and Shoup, 1985; Rutherford et al., 1992; Chiou and Kile, 1994; Rebhun et al., 1992; Pusino et al., 1992). Halogenated hydrocarbons are frequently detected in the soil gas, and thus the sorption of these VOCs in soils has become an active area of research (Steinberg et al., 1987; Smith and Jaffe, 1991; Aochi et al., 1992). Recent studies reported sorption rates and equilibrium data for some chlorinated hydrocarbons (Cabbar et al., 1994) and for benzene (Doğu et al., 1993) by means of a single-pellet moment technique. In low-moisture soils, sorption occurs mainly on mineral surfaces (Chiou and Shoup, 1985; Johnston et al., 1992), but the influence of soil organic matter (SOM) can also be significant (Rebhun et al., 1992). In the current study we use the single-pellet moment method to determine the effect of SOM on dichloromethane sorption in a dry simulated soil.

Method and Experimental Work

Pellets of equal density were made of a natural clay from the Çorum-Hancili region of Turkey. X-ray diffraction analysis indicated that the crystalline fraction of montmorillonite. Pellets with 0.5 to 10.0% humic acid were prepared (Rebhun et al., 1992) by dissolving humic acid (Fluka Chemika) in 55°C water with 0.1 N KOH, and mixing with clay. The pH 8.7 suspension was neutralized to pH 5.8 by adding 1 NH_2SO_4, evaporated to dryness and crushed. A reference clay sample was also prepared by a similar procedure but without adding any humic acid. Cylindrical soil pellets 0.29 cm in length and 1.35 cm in diameter were formed by compression to density 1.4 g/cm^3 in a stainless-steel holder. Carbon content was determined by a Leco CHN elemental analysis instrument (Table 1). Porosity (Table 2) and solid density (2.45 g/cm^3) were measured with a Quantachrome 60 mercury intrusion porosimeter. Solid density determined by a helium pycnometer was slightly higher (2.65 g/cm^3), indicating the presence of pores smaller than radius 1.75 nm not detected by mercury intrusion. Surface area and micropore volume (Table 2) were determined by a Micrometrics ASAP 2000 sorptometer by nitrogen adsorption and desorption.

A compressed cylindrical soil pellet with known physical properties and chemical composition was placed into the single-pellet diffusion cell maintained at 35°C in a chromatograph oven. Doğu and Smith (1975, 1976) and Doğu et al. (1993) provide a detailed description and dimensions of the cell and experimental procedure. Nitrogen carrier-gas streams passed over both end faces of the porous pellet. Adjustment of the pressures at the faces prevented convective transport through the pellet. A 0.5-μL pulse of adsorbing or diffusing volatile organic compound (VOC) was introduced into the stream flowing over one end face, and the response was measured with an FID detector in the stream at the other face. The cell was designed in such a way that the carrier-gas stream containing the tracer passed directly over the upper face of the pellet to create a rapid flow and to eliminate any mass-transfer resistance. As discussed in the previously cited publications (Doğu and Smith, 1975, 1976), neglect of film mass-transfer resistances at the lower and upper faces of the pellet and complete mixing assumption in the lower chamber were justified by keeping the volumes of the chambers sufficiently small and by using sufficiently high flow rates of the carrier-gas streams. In the experiments, flow rate of the upper carrier gas was kept at 1 cm^3/s and lower carrier-gas flow rate was varied.

The low dichloromethane concentrations ensured that adsorption was linear as confirmed by initial experiments with different-sized pulses. Material balances showed that adsorption was reversible. The strength of the input pulse, M, was measured by placing an impermeable Teflon plate over the

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Correspondence concerning this article should be addressed to T. Doğu.

Table 1. Carbon Contents on the Pellets

	Clay–Humic Acid					
Sample	Ref.	S I	S II	S III	S IV	S V
% C	0.05	0.25	1.32	1.64	3.62	5.04

Table 2. Physical Properties of the Pellets

			BJH Surface Area**		Pore Vol.**
Sample	Solid Density ρ_s (g/cm^3)	Porosity* ϵ_p	Nitrogen Desorp. m^2/g	Nitrogen Adsorp. m^2/g	Cumulat. Adsorp. cm^3/g
Reference	2.40	0.42	67.4	44.6	0.169
SI 0.25%C	2.54	0.45	54.6	36.9	0.135
SIII 1.64%C	2.59	0.44	45.2	26.8	0.098
SIV 3.62%C	2.36	0.42	46.2	26.7	0.099
SV 5.04%C	2.47	0.42	37.3	20.6	0.075

*Values are determined by mercury intrusion porosimeter and correspond to pores having radii larger than 1.75 nm.

**Values are determined by sorptometer and correspond to pores having radii between 0.85 and 150 nm.

pellet and determining the area of the response peak leaving the top chamber.

Doğu and Smith (1975, 1976) and Cabbar et al. (1994) discuss overall assumptions of the mathematical model for dynamic response in the single pellet. The zeroth and first absolute-moment expressions are, respectively (Doğu and Smith, 1976; Cabbar et al., 1994; Doğu and Ercan, 1983),

$$m_0 = \frac{M}{1+(L/AD_a)F} \tag{1}$$

and

$$\mu_1 = \frac{m_1}{m_0} = \frac{L^2\epsilon_p}{6D_a}\left(1+\frac{\rho_p K_A}{\epsilon_p}\right)\left(\frac{3(A/L)D_a+F}{(A/L)D_a+F}\right). \tag{2}$$

The variance (second central moment) through the parameter z depends on the mechanism assumed for the sorption rate (Parker and Valocchi, 1986).

$$\mu_2' = \frac{m_2}{m_0} - \mu_1^2$$

$$= \left(\frac{L^2\epsilon_p}{D_a}\right)^2\left(1+\frac{\rho_p K_A}{\epsilon_p}\right)^2\left(\frac{\left(\frac{A}{L}\right)^2+\frac{2}{5}\frac{A}{L}D_aF\frac{1}{15}F^2}{6\left(\frac{A}{L}D_a+F\right)^2}\right)$$

$$+Z\left(\frac{3\left(\frac{A}{L}D_a\right)^2+4\frac{A}{L}D_aF+F^2}{\left(\frac{A}{L}D_a+F\right)^2}\right). \tag{3}$$

For reversible adsorption in monodispersed pores (Model 1) (Doğu and Smith, 1976; Cabbar et al., 1994; Doğu et al., 1986).

$$Z = \frac{L^2\rho_p K_A^2}{3D_a k_a}, \tag{4}$$

where as for fast adsorption in bidispersed pores with micropore diffusion (Model 2) (Neogi and Ruckenstein, 1980; Doğu and Ercan, 1983),

$$Z = \frac{L^2 r_0^2\left(\epsilon_i+\frac{\rho_p K_A}{1-\epsilon_a}\right)^2}{45D_aD_i(1-\epsilon_a)}. \tag{5}$$

Equating Eqs. 4 and 5 yields a relation between the adsorption rate constant, k_a, of Model 1, and the micropore diffusivity, D_i, of Model 2:

$$\rho_p k_a = D_i\frac{15(1-\epsilon_a)(\rho_p K_A)^2}{r_0^2\left(\epsilon_i+\frac{\rho_p K_A}{(1-\epsilon_a)}\right)^2} = D_i\frac{15(1-\epsilon_a)^3}{r_0^2}, \tag{6}$$

where the righthand side approximation is justified for sufficiently large values of $\rho_p K_A$ (for $(\rho_p K_A/(1-\epsilon_a)) \gg \epsilon_i$). The bidispersed pore model refers to pellets formed by agglomeration of micro- or mesoporous grains. Transport through the pellet occurs in the macropores between the agglomerated particles (Doğu et al., 1987), and adsorption occurs in the micropores (Doğu and Ercan, 1983). Though the bidispersed pore model may be more realistic, the reversible adsorption model, by lumping the micropore diffusion process into the rate constant, is somewhat simpler to use.

Results and Discussion

Experimental values of the moments were calculated by numerical integration of the dichloromethane concentration,

$$m_n = \int_0^\infty C_A(L,t)t^n\,dt. \tag{7}$$

Rearranging Eq. 1 shows that plotting M/m_0 vs. flow rate F should yield a straight line with slope L/AD_a and intercept unity. Due to the assumptions involved in writing the bound-

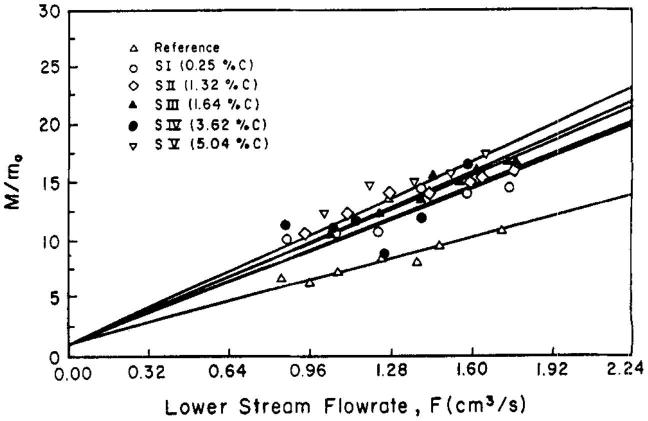

Figure 1. Zeroth-moment data for dichloromethane (T = 35°C).

Table 3. Adsorption and Diffusion Parameters of Dichloromethane on Soil Pellets (T = 35°C)

Sample	Effect. Pellet Diff. D_a (cm^2/s)	Adsorp. Equil. Const. $\rho_p K_A$	Adsorp. Rate Const., $\rho_p k_a$, s^{-1}	D_i/r_0^2 s^{-1}
Reference	0.0356	3,287	Large	
SI (0.25%C)	0.0239	799	14.56	5.24
SII (1.32%C)	0.0224	360	9.81	3.93
SIII (1.64%C)	0.0220	340	8.53	3.24
SIV (3.62%C)	0.0240	284	4.52	1.54
SV (5.04%C)	0.0207	175	3.12	1.07

ary conditions some deviation may be observed from the model predictions at low flow rates. Such plots for pellets of different organic carbon content are shown in Figure 1. Values of effective diffusivities were computed from the slope and are displayed in Table 3. These values corresponding to macropore diffusion coefficients, average to 0.0226 ∓ 0.0012 cm^2/s. For the reference pellet containing no additional organic carbon, a higher value, 0.0356 cm^2/s was obtained.

Adsorption equilibrium constants were evaluated by fitting the first moment data with Eq. 2 as shown in Figure 2. Based on effective diffusivities from the zeroth-moment analysis, $\rho_p K_A$ values were evaluated and are reported in Table 3. The lines of Figure 2 correspond to calculated curves with the D_e and $\rho_p K_A$ values in Table 3.

Fitting second-moment data (Figure 3) with Eq. 3 yielded the adsorption-rate constants for Model 1 shown in Table 3. Adsorption-equilibrium and -rate constants, otherwise comparable to values for VOCs reported by Cabbar et al. (1994), decrease significantly with increase in soil organic content. A possible reason is that adsorption is mainly on the surfaces of clay micropores that can be plugged by organic matter. This explanation is supported by the measured decrease of surface area and micropore volume with increased carbon content (Table 2). With Eq. 6 the quantity D_i/r_0^2 can be calculated for Model 2 and values are reported in Table 3. Grain size of montmorillonite is expected to be less than 2 μm. For an assumed value of $r_0 = 1$ μm, values of D_i decrease from 5.24 $\times 10^{-8}$ cm^2/s for clay with 0.25% carbon to 1.07×10^{-8} cm^2/s for clay with 5.04% carbon. These results are consistent with the explanation that micropores are plugged with soil organic matter.

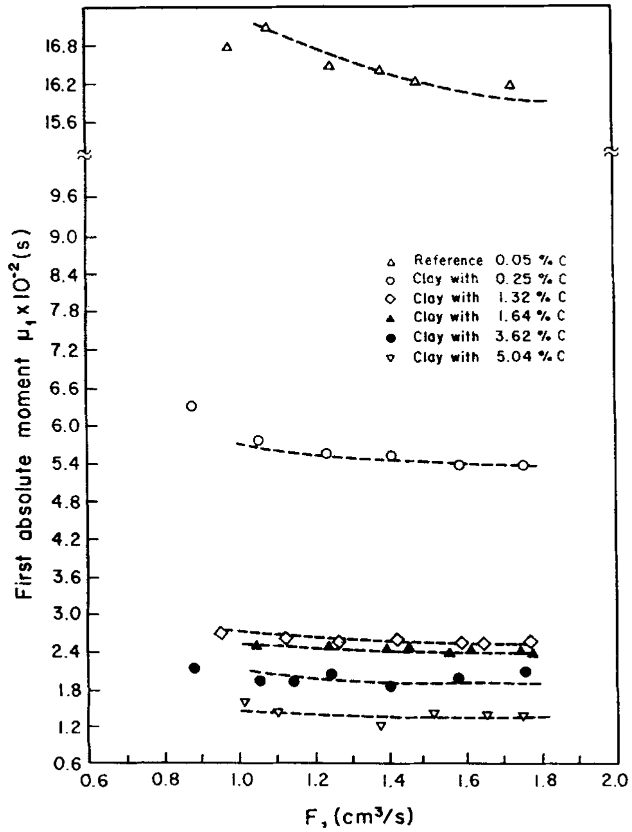

Figure 2. First absolute-moment data for dichloromethane (T = 35°C).

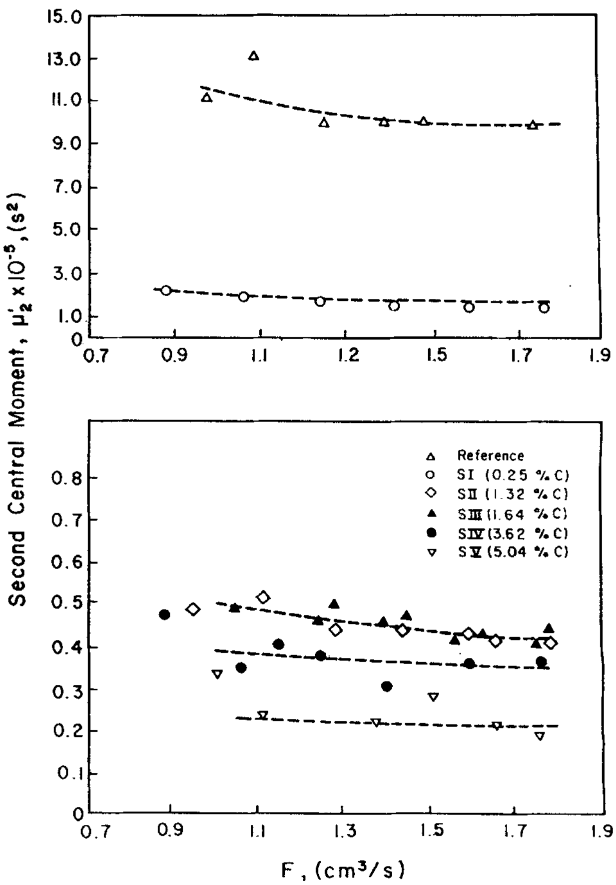

Figure 3. Second central-moment data for dichloromethane (T = 35°C).

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Notation

A = area of end face of pellet, cm^2
C_A = concentration of tracer in the macropores, mol/cm^3

D_a = effective pellet (macropore) diffusivity, cm^2/s
F = lower stream flow rate, cm^3/s
K_A = adsorption-equilibrium constant, cm^3/g
L = length of pellet, cm
r_0 = grain radius, cm
ϵ_a = macroporosity
ϵ_i = microporosity
ϵ_p = total porosity
ρ_p = pellet density, g/cm^3

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