Chloroform Adsorption on Soils

Chao-Hsi Chen

Department of Chemical Engineering, University of Missouri—Columbia, Columbia, Missouri 65211

Nilufer H. Dural*

Department of Civil and Environmental Engineering, Cleveland State University, Cleveland, Ohio 44115

A study involving measurement and analysis of vapor-phase adsorption of chloroform on dry soils was conducted. Experimental adsorption and desorption data were gravimetrically obtained at (15, 20, and 25) °C on two soil samples with different properties. Thermal effects were evaluated through isosteric enthalpy of adsorption and enthalpy curves. The results showed that the adsorption of chloroform on soil was physical adsorption and both adsorbents had energetically heterogeneous surfaces. Equilibrium isotherms were Type II; however, they did not exhibit significant hysteresis upon desorption. Experimental data were correlated by using well-known multilayer isotherm models. The BET model delivered accurate correlations only in the monolayer region, within a deviation range of 1.1% to 4.8%. The GAB equation provided a much better correlation of the entire data set, including mono- and multilayer regions, with error percentages ranging from 1.3% to 4.3%.

Introduction

Subsurface contamination by chlorinated organic compounds, especially low molecular weight hydrocarbons, is of crucial interest. Many of these chemicals, including chloroform, are volatile compounds; thus, their fate may significantly be affected by their vapor-phase sorption on soil.

Adsorption to soil may prevent phototransformation, volatilization, hydrolysis, mobility, and microbial degradation. Many of the investigations on chlorinated organic compounds have focused on their sorption from the aqueous phase to soils, while studies directed toward sorption from the vapor phase to soils are generally limited.[1−9] In soils with moderate to high moisture content, where the competition between water and other sorbate molecules is significant, neglecting vapor-phase sorption may be justified. In dry soils, however, vapor-phase sorption can be important. Therefore, to design effective soil treatment systems and to predict the fate of volatile compounds in the vadose zone, an accurate description of vapor-phase sorption behavior of a volatile contaminant is essential.

The objective of the research presented in this paper was to investigate vapor phase adsorption of chloroform on dry soils. Using two soil samples as adsorbents, adsorption and desorption isotherms were generated at various temperatures to evaluate the thermal and physicochemical effects on the process. The experimental isotherm data were modeled by well-known isotherm equations with the intent to provide input to mathematical models, simulating the transport and fate of volatile organic pollutants in soils.

Experimental Section

Materials. Chloroform was supplied by the Fisher Scientific Co. and Aldrich Co. with a purity of 99.8%. Soil samples from Times Beach, MO, and Visalia, CA, obtained from the Environmental Trace Substances Laboratory, University of Missouri, Rolla, MO, were used as adsorbents. Soil characteristics are given in Table 1; scanning electron microscopy images of the samples are shown in Figures 1 and 2. Prior to their use, the samples were further characterized with respect to specific surface area and pore size through BET analysis by using nitrogen gas at the liquid nitrogen temperature (−195.8 °C). The results of the physical characterization are presented in Table 2.

Table 1. Soil Characteristics

	Missouri soil	California soil
clay, %	33.4	21.7
silt, %	52.7	35.2
sand, %	11.4	45.1
organic matter, %	2.4	1.7
pH	6.9	8.1

Table 2. Surface Properties of the Soil Samples

	Missouri soil	California soil
specific surface area, $m^2 \cdot g^{-1}$	44.14	25.33
average pore diameter, Å	17.69	16.00
total pore volume, $cm^3 \cdot g^{-1}$	0.02	0.01
median pore diameter[a], Å	24.46	17.67

[a] This value is based on pore volume.

Methods. Adsorption and desorption isotherm data at (15, 20, and 25) °C were measured gravimetrically using a Cahn-2000 electrobalance (CAHN Instruments) mounted in a glass vacuum chamber assembly. The C-2000 electrobalance is a very sensitive mass and force measurement instrument, which is designed for masses up to 3.5 g and sensitive to changes as small as 0.1 μg. A schematic of the apparatus is shown in Figure 3. A detailed description is given elsewhere.[2] The adsorption temperature was controlled to ±0.1 °C of the desired operating temperature. A vacuum of approximately 6.1×10^{-4} kPa was obtained and the leak rate of the whole system was 2.7×10^{-4} kPa h^{-1}.

After the electrobalance was zeroed and calibrated, approximately 50 mg of soil sample was placed on the

---

* To whom correspondence should be addressed.

10.1021/je010313p CCC: $22.00

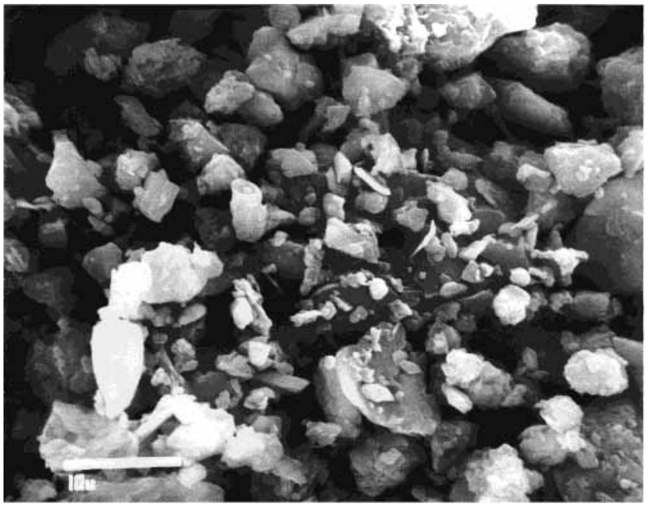

Figure 1. Scanning electron micrograph of a Missouri soil sample (magnification 2200×).

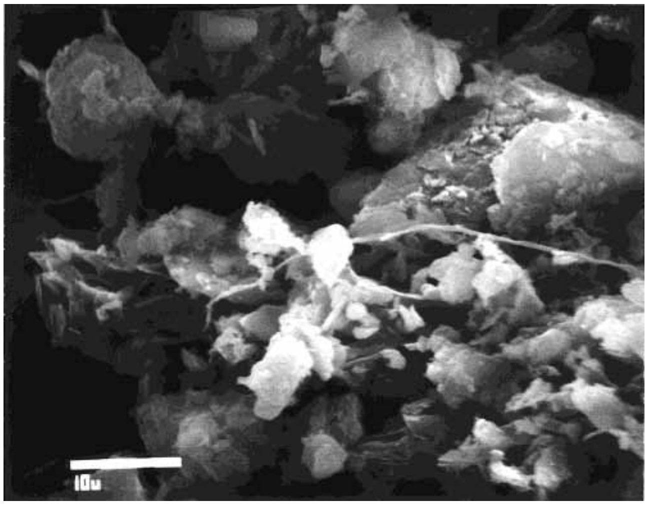

Figure 2. Scanning electron micrograph of a California soil sample (magnification 2200×).

hangdown pan and regenerated to remove moisture. The regeneration was carried out by evacuating the system and applying heat at 70 °C until a constant sample mass was obtained. Typically, this procedure required 10 h or longer.

Following regeneration, the soil sample was cooled to the adsorption temperatures of (15, 20, and 25) °C, and the chloroform vapor was introduced into the system. The mass change of the sample due to adsorption of the chloroform vapor was monitored by the electrobalance and a recorder. After equilibrium was reached, as indicated by a constant sample mass, the system pressure and the sample mass were recorded. Then, more chloroform vapor was introduced into the system, and the procedure was repeated for a new system pressure. Equilibrium isotherm data were taken from very low pressure up to about 90% of the saturation pressure at (15, 20, and 25) °C. Following adsorption, desorption measurements were made by reducing the system pressure in steps. Then, a fresh soil sample was used to acquire a new set of adsorption isotherm data, and the entire experimental process was repeated.

Results and Discussion

Vapor-phase adsorption isotherms of chloroform on the test soils were obtained at (15, 20, and 25) °C. The reversibility was investigated by carrying out complete adsorption−desorption cycles on selected pairs. For both chloroform−soil pairs examined, the isotherms were Type II,[10] signifying the formation of multiple layers of chloroform molecules on the soil particle surface. However, they did not exhibit significant hysteresis upon desorption. The adsorption and desorption isotherm data of chloroform on the Missouri soil sample at 15 °C are shown as a typical illustration in Figure 4. The isotherms were expressed in the standard manner, namely, the amount of chloroform vapor adsorbed per gram of dry soil (W) as a function of the equilibrium pressure, P, or the relative pressure, P_r($=P/P_0$), where P_0 is the saturation pressure. The monolayer region, as indicated by the initial convex region of the curve, typically ended at an approximate relative pressure (P_r) of 0.4. The sharp rise of the isotherm at the higher values of the relative pressure was because of multilayer adsorption on the surface of the soil sample. The reproducibility of the results was investigated selectively by conducting two consecutive adsorption measurements with chloroform vapor on fresh soil samples. As illustrated in Figure 5, several data points were reproduced within the limits of the experimental error. The experimental adsorption and desorption equilibrium values and the reproduced data sets are presented in Tables 3 and 4.

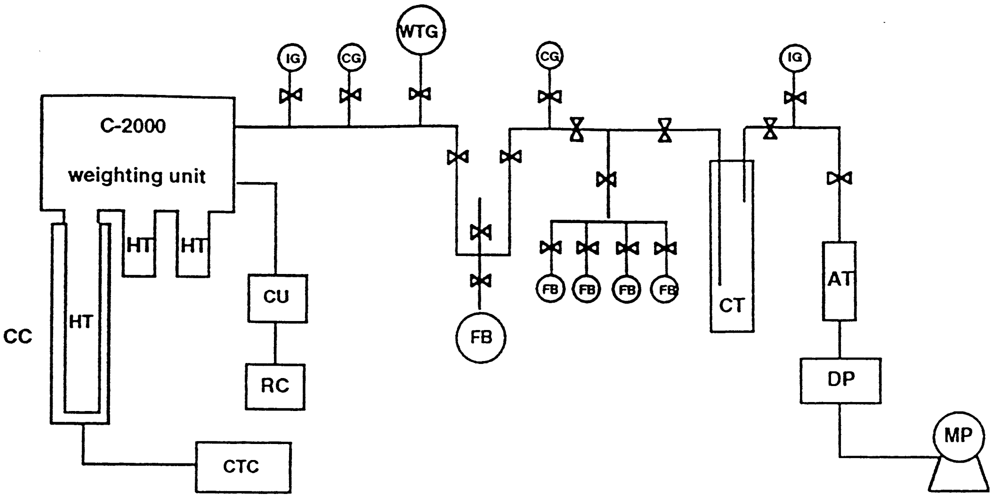

Figure 3. Schematic representation of the adsorption apparatus. CC, copper coil; HT, hangdown tube; CU, electrobalance control unit; RC, recorder; CTC, constant temperature circulator; IG, ionization gauge; CG, convectron gauge; WTG, Wallace and Tiernan gauge; FB, feed bottle; CT, cold trap; AT, activated carbon trap; DP, diffusion pump; MP, mechanical pump.

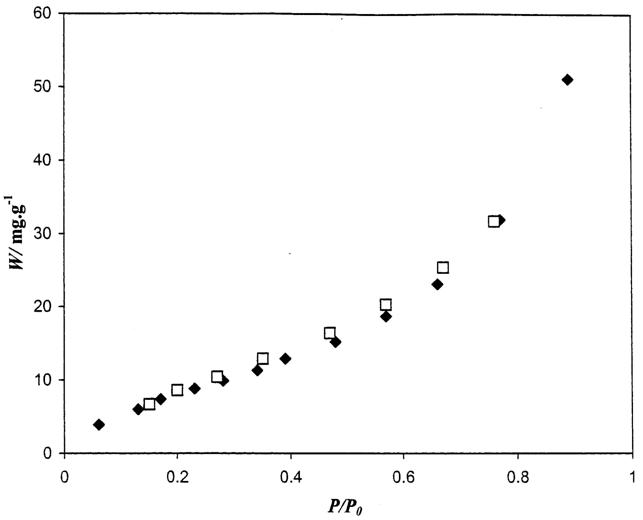

Figure 4. Adsorption and desorption of chloroform vapor (Missouri soil sample, 15 °C). (◆) adsorption; (□) desorption.

Table 3. Adsorption Equilibrium Data for Chloroform Vapor on California Soil Sample

		adsorption			adsorption		desorption	
		P	*W*		*P*	*W*	*P*	*W*
temperature		kPa	mg/g		kPa	mg/g	kPa	mg/g
15 °C	set I	0.2	0.5	set II	0.9	1.1	9.1	13.0
(P_0 = 16.7 kPa)		1.0	1.5		1.8	1.8	7.5	10.7
		2.1	2.7		2.2	2.1	6.2	8.9
		3.2	4.0		3.2	2.6	4.3	6.9
		4.3	5.1		4.3	3.3	2.3	4.0
		5.4	6.5		5.3	4.4	1.2	3.1
		6.4	8.0		6.4	5.3	0.5	2.0
		7.3	9.2		7.3	6.1	0.3	1.6
		8.2	10.5		8.9	7.5		
		10.0	13.0		11.2	10.5		
		12.0	18.1		13.1	15.8		
		14.3	34.8		15.0	33.0		
		16.1	101.4		16.0	92.6		
20 °C	set I	0.6	1.3				15.30	18.5
(P_0 = 21.0 kPa)		1.3	2.0				13.26	14.2
		2.6	3.2				10.16	9.9
		3.7	4.1				7.25	7.2
		4.7	5.1				5.15	5.6
		5.8	6.6				2.97	3.4
		6.8	7.5				1.69	2.3
		7.6	8.6				0.57	1.4
		8.9	9.7					
		10.4	11.3					
		12.1	12.9					
		14.0	15.8					
		15.7	19.5					
		17.3	25.8					
		18.9	41.2					
25 °C	set I	0.8	1.6	set II	0.9	2.2		
(P_0 = 26.2 kPa)		1.9	3.4		2.0	3.7		
		2.8	4.2		3.1	5.0		
		3.9	5.6		4.2	6.0		
		4.7	6.3		5.3	6.8		
		5.9	7.1		6.4	7.6		
		6.9	7.9		7.3	8.3		
		7.8	8.6		8.3	9.0		
		8.9	9.5		9.4	9.8		
		10.5	10.7		10.9	11.0		
		12.3	12.2		12.2	12.0		
		14.0	13.9		13.7	13.5		
		15.6	15.7		15.1	14.9		
		17.0	17.5		17.0	17.1		
		18.8	18.4		18.9	18.6		

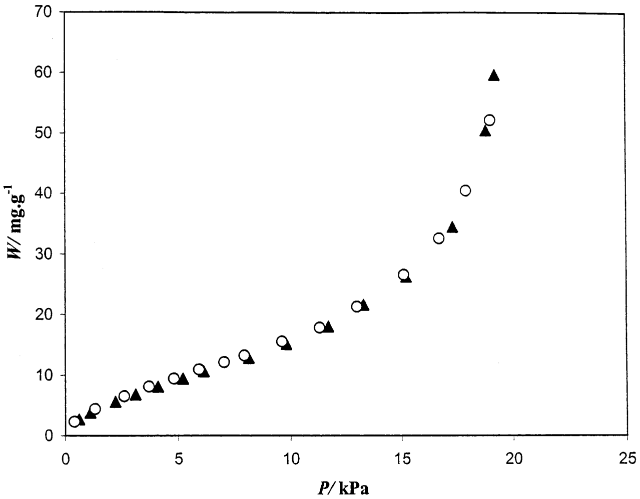

Figure 5. Reproduced adsorption isotherm data for chloroform vapor (Missouri soil sample, 20 °C). (▲) set I; (○) set II.

Table 4. Adsorption/Desorption Equilibrium Data for Chloroform Vapor on Missouri Soil Sample

		adsorption			adsorption		desorption	
		P	*W*		*P*	*W*	*P*	*W*
temperature		kPa	mg/g		kPa	mg/g	kPa	mg/g
15 °C	set I	1.0	3.9	set II	0.5	2.8	12.7	31.7
(P_0 = 16.7 kPa)		2.2	6.0		1.7	5.5	11.2	25.4
		2.9	7.4		2.8	7.5	9.5	20.3
		3.9	8.8		3.9	9.3	7.9	16.4
		4.7	9.9		4.9	11.0	5.9	12.9
		5.6	11.3		5.8	12.5	4.5	10.4
		6.5	12.9		6.7	13.9	3.4	8.6
		8.0	15.2		7.6	15.3	2.5	6.7
		9.5	18.7		9.3	19.2		
		11.0	23.1		10.8	23.5		
		12.9	31.9		12.7	31.1		
		14.8	51.1		14.3	44.1		
					15.3	78.8		
20 °C	set I	0.6	2.7	set II	0.4	2.3		
(P_0 = 21.0 kPa)		1.1	3.8		1.3	4.4		
		2.2	5.6		2.6	6.5		
		3.1	6.8		3.7	8.1		
		4.1	8.1		4.8	9.4		
		5.2	9.4		5.9	10.9		
		6.1	10.6		7.0	12.1		
		8.1	12.8		7.9	13.2		
		9.8	15.1		9.6	15.5		
		11.7	18.0		11.3	17.8		
		13.3	21.6		13.0	21.3		
		15.2	26.3		15.1	26.6		
		17.3	34.5		16.7	32.6		
		18.8	50.5		17.9	40.5		
		19.2	59.7		19.0	52.2		
25 °C	set I	0.8	3.1	set II	0.8	1.8		
(P_0 = 26.2 kPa)		1.1	3.6		1.6	3.8		
		2.2	5.1		2.5	5.0		
		3.2	6.0		3.8	7.2		
		4.2	7.2		4.3	7.9		
		5.3	8.1		5.4	8.8		
		6.3	9.4		6.5	9.7		
		8.3	11.0		8.5	10.8		
		8.8	11.7		9.9	12.8		
		10.6	13.4		11.2	13.8		
		12.3	15.2		13.1	15.6		
		14.4	17.7		14.6	17.4		
		16.1	19.9		15.9	18.9		
		17.9	22.8		16.8	20.3		
		19.9	26.5		18.2	22.3		
					19.4	24.3		

Experimental data were correlated by the BET[10] and the GAB[11−13] multilayer isotherm models. The BET equation includes the basic assumptions of the Langmuir isotherm with the exceptions that multilayer adsorption occurs and

Table 5. Model Predictions for Vapor-Phase Chloroform Adsorption on Soil

		BET ($P_r < 0.4$)			GAB (entire set)			
soil type	t (°C)	W_m (mg·g^{-1})	C	% error	W_m (mg·g^{-1})	C	k	% error
California	15	7.06	14.79	4.84	7.96	12.23	0.93	4.27
	20	7.25	10.95	3.60	7.41	12.41	0.95	3.55
	25	7.61	9.10	1.51	10.34	7.40	0.72	2.61
Missouri	15	8.84	10.51	1.33	9.61	9.44	0.93	1.29
	20	9.01	10.91	1.38	10.38	9.66	0.87	1.69
	25	8.91	11.97	3.13	10.55	10.54	0.83	3.02

the heat of adsorption for the first layer is different from the value for all succeeding layers. The final BET equation has the following form,

$$\frac{W}{W_m} = \frac{CP_r}{(1 - P_r)(1 - P_r + CP_r)} \qquad (1)$$

where P_r is the relative pressure, W is the adsorption equilibrium uptake, W_m is the monolayer capacity, and C is a constant related to the net enthalpy of adsorption as follows:

$$C = C_0 \exp[(q_1 - q_L)/RT]; \quad C_0 \approx 1.0 \qquad (2)$$

In eq 2, q_1 and q_L are the enthalpy of adsorption of the first layer and the enthalpy of liquefaction of the adsorbate, respectively, T is the absolute temperature, and R is the universal gas constant.

The GAB model, which was developed in independent studies by Anderson,[11] De Boer,[12] and Guggenheim,[13] is an improvement over the BET model regarding the multilayer region. The model is based on the assumption that the enthalpy of adsorption of the second to approximately ninth layers, q_2, differs from the enthalpy of liquefaction, q_L, by a constant amount, and that the enthalpy of adsorption is equal to the enthalpy of liquefaction in the layers following these. The resulting equation for the GAB model is

$$\frac{W}{W_m} = \frac{CkP_r}{(1 - kP_r)(1 - kP_r + CkP_r)} \qquad (3)$$

where all terms are the same as defined in the BET equation. The additional parameter k is related to the difference between the enthalpy of adsorption of the multilayers and the enthalpy of liquefaction. It is primarily a measure of the attractive forces and can be expressed as

$$k = k_0 \exp[(q_1 - q_2)/RT] \qquad (4)$$

A comparison of the theoretical isotherms predicted by the BET and the GAB equations with the experimental data is illustrated for the Missouri soil sample at 25 °C in Figure 6, as a typical example. The complete results of the data correlation using the BET and GAB models, including the average percentage deviations of the predicted isotherms from the experimental ones, are presented in Table 5. The best fit model parameters given in the table were obtained by using a nonlinear regression analysis. The error percentages were calculated from the following expression,

$$\text{% deviation} = \frac{U_E - U_t}{U_E} \times 100 \qquad (5)$$

where U_E and U_t are experimental and theoretical uptake values, respectively.

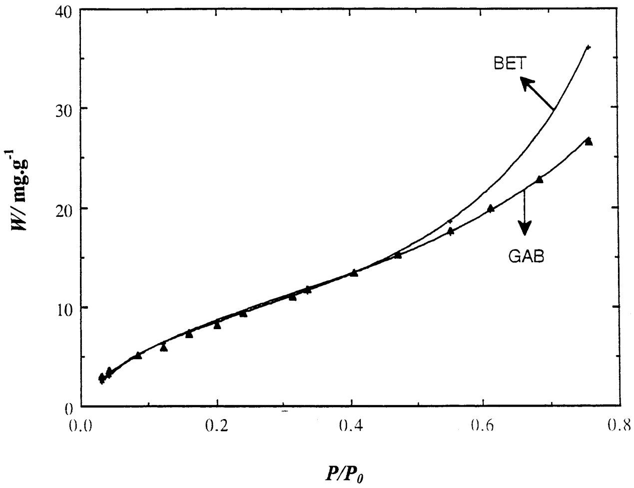

Figure 6. Comparison of model predictions (Missouri soil sample, 25 °C). (▲) experimental.

In the monolayer region ($P_r < 0.4$), the BET equation fitted the experimental data very well, within a deviation range of 1.1% to 4.8%. However, the equilibrium uptakes predicted by the BET model in the multilayer region were significantly higher than the experimental values. The average absolute percentage deviation for the entire pressure range was typically >15%, and as the pressure increased, the deviation also increased. The GAB model provided superior overall predictions than did the BET equation. The average absolute percentage deviations for the entire relative pressure range were in an acceptible range, varying from 1.3% to 4.3%. The soil monolayer capacities (W_m) for chloroform obtained from both models clearly showed that the Missouri soil sample had a larger capacity (Table 5). The value of W_m, as determined by the GAB equation, varied from (9 to 40)% higher than that predicted by the BET equation.

The experimental data were also correlated by the Polanyi Potential[14] model to obtain a temperature-independent interpretation of the data. The Polanyi theory assumes that the adsorbent exerts long-range attractive forces on the gas or vapor surrounding it. These forces give rise to a potential field with the potential decreasing as the distance from the adsorbent surface increases. The adsorption potential, ϵ, is given by

$$\epsilon = -RT \ln(f/f_0) = -RT \ln(P/P_0) \qquad (6)$$

where f_0 and P_0 refer to the saturation fugacity and pressure for the liquid sorbate and f and P are the corresponding equilibrium quantities for the adsorbed phase; R is the universal gas constant. A unique temperature-independent relationship between the adsorption potential and the volume of adsorbed species exists for a given adsorbate−adsorbent system. In other words, a plot of the volume adsorbed versus the adsorption potential should yield a temperature-independent curve that is called

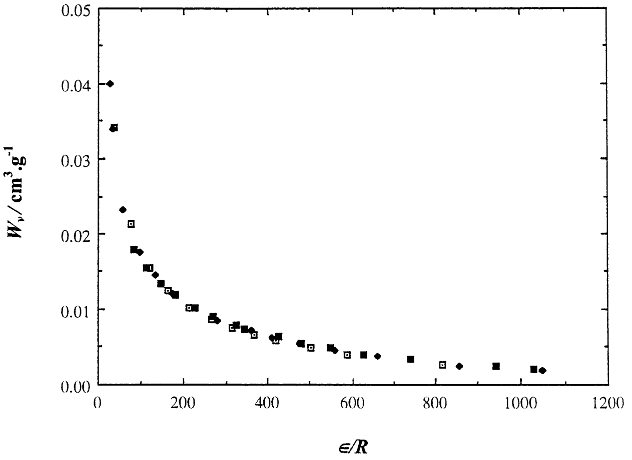

Figure 7. Characteristic curve for chloroform vapor on the Missouri soil sample. (⊡) 15 °C; (◆) 20 °C; (■), 25 °C.

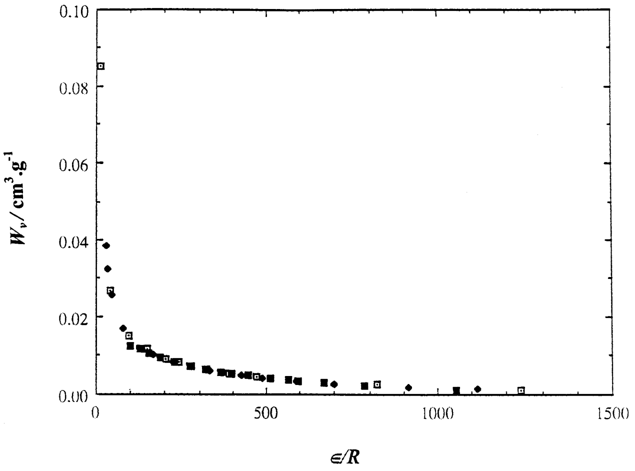

Figure 8. Characteristic curve for chloroform vapor on the California soil sample. (⊡) 15 °C; (◆) 20 °C; (■) 25 °C.

the characteristic curve. Construction of the characteristic curve is a practical approach for summarizing vapor-phase adsorption data over a wide range of temperatures. Provided that a soil−pollutant system follows the potential theory, this characteristic curve can be used to predict the seasonal adsorption capacities of soils. The characteristic curves of chloroform on Missouri and California soil samples, plotted as cm^3 of chloroform adsorbed/g of soil versus ϵ/R (i.e, $T \ln(P_0/P)$) are shown in Figures 7 and 8. As illustrated, the equilibrium data for all temperatures fall into a single curve; thus, they can be extrapolated or interpolated to forecast the sorption capacities of the test soils for chloroform at other temperatures.

The difference in the independently measured specific surface areas of the soil samples (Table 2) is reflected on the isotherms. Values of the chloroform uptake corresponding to a given equilibrium pressure were always higher on the Missouri soil sample, particularly in the monolayer region. This trend can be observed from the monolayer values shown in Table 5. In Figure 9, adsorption of chloroform vapor at 25 °C by the two soil samples is compared. At other temperatures, similar behavior is observed.

It is well established that the clay minerals and the organic matter provide most of the surface area.[15] However, soil organic matter is the major soil sorbent for organic substances under saturated conditions;[3] while clay minerals contribute significantly toward the specific surface area in dry soils.[9] The experimental conditions and data support the hypothesis that the higher level of chloroform adsorption on the Missouri soil sample is primarily due to its higher clay content.

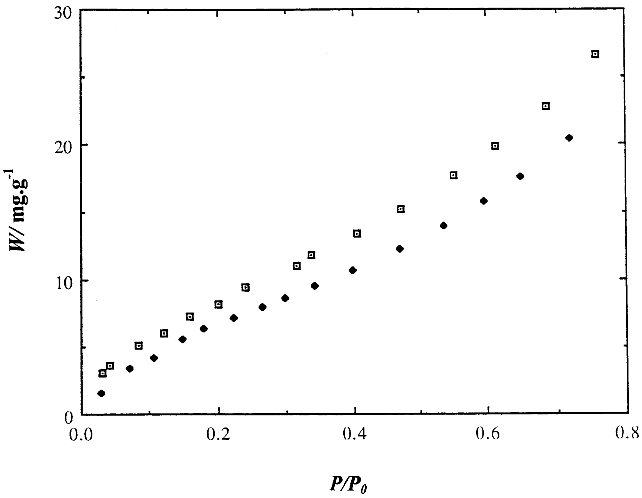

Figure 9. Comparison of chloroform vapor adsorption on different soil samples at 25 °C. (⊡) Missouri soil; (◆) California soil.

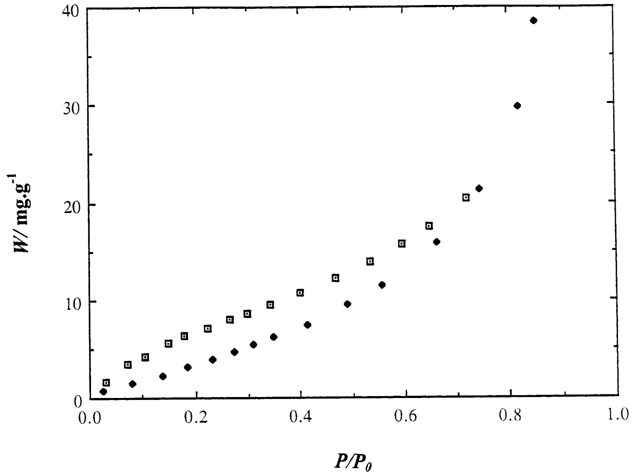

Figure 10. Comparison of chloroform and carbon tetrachloride adsorption (California soil sample, 25 °C). (⊡) chloroform; (◆) carbon tetrachloride.[2]

With use of the results of a previous study on carbon tetrachloride vapor conducted by the authors,[2] vapor-phase adsorption of chloroform and carbon tetrachloride on the California soil sample at 25 °C are compared in Figure 10. As can be observed, the equilibrium uptake of the soil for chloroform is essentially higher than that of carbon tetrachloride. This indicates a positive effect of adsorbate polarity on clay mineral adsorption and is consistent with the observations made by Chiou and Shoup[9] on mono-, di-, and trichlorobenzene adsorption.

Isotherms generated at (15, 20, and 25) °C provided data that were used to estimate the isosteric enthalpy of adsorption. As anticipated, increasing the temperature resulted in a downward shift of the isotherms. This effect is illustrated in Figure 11. Isosteric enthalpy of adsorption at constant loading, ΔH_{ads}, was estimated using the Clasius−Clapeyron equation:

$$\Delta H_{\mathrm{ads}} = R[\partial \ln P/\partial(1/T)]_{\mathrm{M}} \qquad (7)$$

Figure 12 shows the isosteric enthalpies of adsorption for the two soils, plotted as a function of the amount of

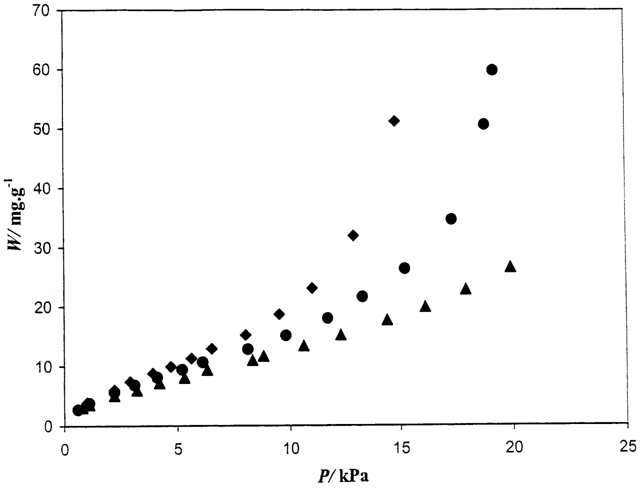

Figure 11. Effect of temperature on the chloroform vapor adsorption (Missouri soil sample). (◆) 15 °C; (●) 20 °C; (▲) 25 °C.

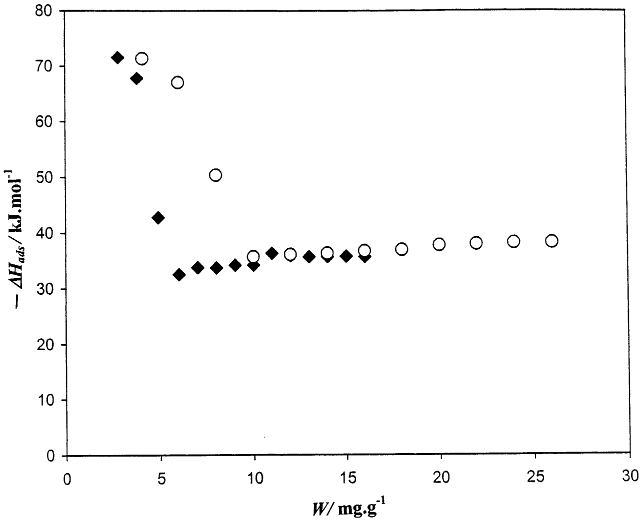

Figure 12. Variation of isosteric enthalpy of adsorption with increasing chloroform adsorption on the soil samples. (◆) California soil sample; (○) Missouri soil sample.

chloroform vapor adsorbed (enthalpy curves). Enthalpy of adsorption is a differential quantity that is directly related to the energy of interaction between the adsorption sites and adsorbate molecules. An energetically heterogeneous surface, such as soil, posseses sites with different adsorption potentials that lead to a variation in the isosteric enthalpy of adsorption at different loadings, particularly in the monolayer region where the adsorbate is in direct contact with the adsorbent.[14,16] On such surfaces, adsorption initially takes place on the most active sites, resulting in the highest interaction energy. As these sites are filled, adsorption continues on the less active sites, giving rise to a lower amount of energy. Therefore, a plot of isosteric enthalpy of adsorption as a function of adsorbate loading usually exhibits a steep drop, in magnitude, in the monolayer region. As the multilayers are formed, adsorption is primarily due to the interaction between the adsorbed-state and the free-state adsorbate molecules. Thus, the curve levels off. In this region, formation of multiple layers is comparable to the condensation of the adsorbate molecules, and the enthalpy of adsorption becomes pretty much like the enthalpy of condensation. Results of the present work, presented in Figure 12, are in complete agreement with this theoretical foundation. They also confirm that the adsorption of chloroform vapor on soils is basically physical adsorption and completely reversible. In the monolayer region, magnitudes of the enthalpy of adsorption at various loadings on the Missouri soil are higher than those on the California soil. This is believed to be essentially the result of the higher clay content of the Missouri soil and implies a higher energy requirement for its decontamination through in situ desorption technologies.

Conclusions

Vapor-phase adsorption and desorption equilibrium data of chloroform on dry soils were measured and analyzed. The isotherms were of Type II, sigmoidal in shape as an indication of multilayer adsorption. Hysteresis between the adsorption and desorption cycles was not significant. In comparison to carbon tetrachloride, chloroform vapor adsorption was higher. This was attributed to the polarity effect on the adsorption of organic vapors on dry soils. The sorption capacity for chloroform was positively correlated with the clay contents of the test soils, which, in turn, reflected the difference in their specific surface areas. Increasing the temperature resulted in a decrease in the soil's sorption uptake. The values of isosteric enthalpy of adsorption were of the same order of magnitude as the heat of liquefaction of chloroform. This confirmed that the adsorption of chloroform on dry soils was essentially due to physical forces and completely reversible.

Literature Cited

(1) Peng, D.; Dural, N. H. Multicomponent Adsorption of Chloroform, Carbon Tetrachloride, and Trichloroethane on Soils. *J. Chem. Eng. Data* **1998**, *43*, 283−288.

(2) Dural, N. H.; Chen, C. H.; Puri, R. K. Adsorption Equilibrium of Carbon Tetrachloride on Dry Soils. *Chem. Eng. Commun.* **1997**, *162*, 75−92.

(3) Ong, S. K.; Lion, L. W. Effects of Soil Properties and Moisture on the Sorption of Trichloroethylene Vapor. *Water Res.* **1991**, *25*, 29−36.

(4) Chiou, C. T.; Kile, D. E.; Malcolm, R. L. Sorption of Vapors of Some Organic Liquids on Soil Humic Acid and Its Relation to Partitioning of Organic Compounds in Soil Organic Matter. *Environ. Sci. Technol.* **1988**, *22*, 298−303.

(5) Poe, S. H.; Valsaraj, K. T.; Thibodeaux, L. J.; Springer, C. Equilibrium Vapor Phase Adsorption of Volatile Organic Chemicals on Dry Soils. *J. Hazard. Mater.* **1988**, *19*, 17−32.

(6) Smith, J. A.; Chiou, C. T.; Kammer, J. A.; Kile, D. E. Effect of Soil Moisture on the Sorption of Trichloroethylene Vapor to Vadose Zone Soil at Picatinny Arsenal, New Jersey. *Environ. Sci. Technol.* **1990**, *24*, 676−683.

(7) Koo, J. K.; Ahn, D. W.; Yoon, S. P.; Kim, D. H. Effects of Water Content and Temperature on Equilibrium Distribution of Organic Pollutants in Unsaturated Soil. *Water, Air, Soil Pollut.* **1990**, *53*, 267−277.

(8) Silva, J. A. K.; Bruant, R. G.; Conklin, M. H.; Corley, T. L. Equilibrium Partitioning of Chlorinated Solvents in Vadose Zone. *Environ. Sci. Technol.* **2002**, *36*, 1613−1619.

(9) Chiou, C. T.; Shoup, T. D. Soil Sorption of Organic Vapors and Effects of Humidity on Sorptive Mechanism and Capacity. *Environ. Sci. Technol.* **1985**, *19*, 1196−1200.

(10) Brunauer, S. P.; Emmett, H.; Teller, E. Adsorption of Gases in Multimolecular Layers. *J. Am. Chem. Soc.* **1938**, *60*, 309−319.

(11) Anderson, R. B. Modifications of Brunauer, Emmett and Teller Equation. *J. Am. Chem. Soc.* **1946**, *68*, 686−691.

(12) De Boer, J. H. *The Dynamical Character of Adsorption*; Clarendon Press: Oxford, 1953.

(13) Guggenheim, E. A. *Applications of Statistical Mechanics*; Clarendon Press: Oxford, 1966.

(14) Ruthven, D. M. *Principals of Adsorption and Adsorption Processes*; John Wiley: New York, 1984.

(15) Bohn, H. L.; Prososki, G. K.; Echardt, J. G. Hydrocarbon Adsorption by Soils as the Stationary Phase of Gas−Solid Chromatography. *J. Environ. Qual.* **1980**, *9*, 563−565.

(16) Young, D. M.; Crowell, A. D. *Physical Adsorption of Gases*; Butterworths: London, 1962.

Received for review November 20, 2001. Accepted May 23, 2002.

JE010313P