Analysis of vapor phase adsorption equilibrium of 1,1,1-trichloroethane on dry soils [1]

Nilufer H. Dural [a,*], Chao-Hsi Chen [b]

[a] *Department of Chemical Engineering, Cleveland State University, Cleveland, Ohio 44115, USA*
[b] *Department of Chemical Engineering, University of Missouri-Columbia, Columbia, Missouri 65211, USA*

Abstract

The migration and fate of volatile organic pollutants in soils are highly dependent on their vapor-phase sorptive behavior. The objective of the research presented in this paper was to investigate the vapor-phase adsorption/desorption equilibrium of 1,1,1-trichloroethane (TCA) on dry soils. A gravimetric adsorption apparatus was developed and used to generate adsorption/desorption isotherms of TCA at 288, 293 and 298 K on two soil samples, obtained from Visalia–California and Times Beach–Missouri, with different physical/chemical characteristics. The influences of temperature and soil properties were investigated. Isosteric heats of adsorption were calculated and heat curves were established. The experimental data were correlated by well-known vapor phase isotherm models including the Polanyi Potential, the BET, and the GAB models.

Equilibrium isotherms of TCA on both soils were Type II, characterizing vapor condensation to form multilayers, and they exhibited hysteresis upon desorption. A positive correlation between the soil's specific surface area and its sorption capacity was observed. Clay content and pore size were also dominating factors. Thermal data showed that the adsorption of TCA vapor on soil was primarily due to physical forces and both samples exhibited energetically heterogeneous surfaces. Results followed the Potential Theory satisfactorily and led to a single temperature-independent characteristic curve for each soil–TCA pair. The BET model gave an accurate data fit for up to 40% of the saturation pressure, while the GAB model provided a superior fit of the data for the entire relative pressure range. © 1997 Published by Elsevier Science B.V.

Keywords: Adsorption; Vapor; 1,1,1-Trichloroethane; Soil; Volatile organic pollutant

---

1. Introduction

Chlorinated volatile organic compounds constitute a major class of subsurface contaminants, although they are widely used as solvents and degreasing agents by numerous industries and the military. It is estimated that of the chlorinated solvents that have been used as degreasers across the U.S., 60% has been 1,1,1-trichloroethane (TCA), which is also known as methyl chloroform [1]. In addition to being an ozone-depleting chemical, spent TCA is a listed hazardous waste, and it has been designated as a priority pollutant contaminating soil and ground water in several regions.

The transport, fate and removal of organic pollutants in soils are highly dependent upon their sorptive behavior. Therefore, an accurate description of the sorption behavior of a contaminant is important. The focus of the preponderance of research on halogenated organic compounds has been on the sorption from the aqueous or nonaqueous liquid phase to soils [2–4]. Studies including sorption from the gas phase to soils are generally lacking. Many chlorinated solvents, including 1,1,1-trichloroethane, are volatile compounds that pass through the soil as a vapor. In some situations, where the solid-phase exchange is highly mediated by a wetting aqueous phase in soils, neglecting vapor-phase sorption may be justified. In the unsaturated zone, however, particularly in dry soils, gas-phase sorption can be significant. To develop adequate treatment and control for volatile air emissions, and to predict the fate of volatile compounds in the unsaturated zone, analysis of the important factors involved in the vapor-phase sorption processes is necessary.

Depending on the complex nature of the soil organic matter and mineralogical composition, the sorption characteristics of different soils may vary widely. A remarkably good relationship has been found between the organic matter content of soils and their capacities to sorb most organic chemicals [5]. Current knowledge of the sorption of hydrophobic organic compounds points out that adsorption capacity is controlled by the amount of organic content of the soil under saturated conditions [2]. By contrast, in the absence of water, the sorption process was suggested to be dominated by the mineral fraction of the soil [6,7]. Furthermore, because adsorption is a surface phenomenon, the uptake capacity of a specific adsorbent (soil) is dependent upon its specific surface area and its pore size distribution, as well as the size of the adsorbate molecule. Hence, the analysis of the adsorption process for a pollutant–soil system should include the impact of the soil characteristics mentioned above.

Earlier research suggests that the temperature of the soil system must be given serious consideration [2,8–10]. In gas-phase adsorption, the pollutant molecules are bound to the soil surface by several mechanisms, including van der Waals forces, hydrogen bonding and electrostatic interactions. The binding energy is a function of temperature, increasing with decreasing temperature in the case of physical adsorption. Thus, a change in soil temperature, resulting from climatic changes and depth, may cause varying soil sorption capacities for a specific pollutant. Traditionally, the temperature dependence of adsorption facilitates the measurement of thermodynamic properties such as the heat of adsorption.

The present work was undertaken with the goal of analyzing the vapor-phase adsorption/desorption of 1,1,1-trichloroethane by dry soils. Equilibrium isotherms were

generated on two soil samples with different physical/chemical properties and at three different temperatures in order to examine and quantify the influence of temperature and soil characteristics on the process. This, in turn, would provide information with regard to the pollutant's migration in and removal from the soil. The experimental data were modeled by the well-known vapor-phase, multilayer isotherm equations as input to fate and transport models predicting the degradation or movement of TCA in unsaturated soils.

2. Materials and methods

2.1. Materials

1,1,1-trichloroethane was supplied by the Aldrich Co. with a purity of 99 + %. The soil samples from Visalia–California (1.7% organic matter, 45.1% sand, 35.2% silt, 21.7% clay) and Times Beach–Missouri (2.4% organic matter, 11.4% sand, 52.7% silt, 33.4% clay) were used as adsorbents. Scanning electron micrographs of the soil samples are shown in Figs. 1 and 2. Prior to their use, the samples were further characterized with respect to specific surface area and pore size by using an automated BET sorptometer (Porous Materials, Inc.) and nitrogen gas at liquid nitrogen temperature (− 195.8°C). The results of the physical characterization are presented in Table 1.

2.2. Apparatus

The adsorption and desorption data were measured gravimetrically using a Cahn-2000 electrobalance (CAHN Instruments), with a sensitivity of 0.1 μg, mounted in a glass

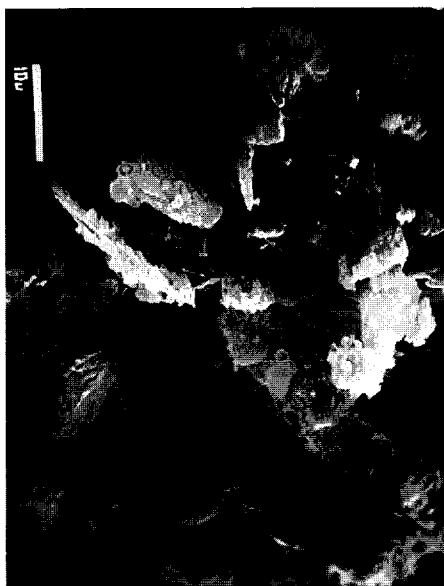Fig. 1. Scanning electron micrograph of Missouri soil sample (magnification × 2200).

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

vacuum chamber assembly. The adsorption apparatus was assembled to contain the Cahn-2000 electrobalance, the pressure gauges, the temperature controller, and the vacuum system. The electrobalance was placed in a vacuum bottle and the assembly was equipped with hangdown tubes for the sample and counterweight pails. The sample weight was monitored with a strip chart recorder connected to the electrobalance control unit. The sample hangdown tube was wrapped in a copper circulation coil connected to a refrigerated/heated constant temperature circulator with a temperature control within ±0.02°C of the set point. The sorption temperature was monitored by a thermocouple connected to a digital thermometer with an accuracy of ±0.1°C. The vacuum system consisted of a mechanical pump for roughing, a diffusion pump for high vacuum, and a dry ice sorption trap. A vacuum of approximately 4.6×10^{-3} mm Hg was obtained and the leak rate of the whole system was 0.002 mm Hg/h. In order to prevent the 1,1,1-trichloroethane vapor from being discharged into the outdoors from the vent, an

Table 1
Physical characteristics of the soil samples

	Missouri soil	California soil
Specific surface area m^2/g	44.14	25.33
Average pore diameter, Å	17.69	16.00
Total pore volume, cm^3/g	0.02	0.01
Median pore diameter [a], Å	24.46	17.67

[a] This value is based on pore volume.

activated carbon trap was set up between the dry ice sorption trap and the vacuum pump. Two convection gauges were used to monitor the pressure during evacuation. Equilibrium pressures were measured with a Wallace and Tiernan absolute pressure gauge. A schematic diagram of the experimental apparatus is shown in Fig. 3.

2.3. Procedure

After the electrobalance was zeroed and calibrated, a 55 mg soil sample was placed on the hangdown pan suspended from the electrobalance. The regeneration was carried out by evacuating the system and applying heat at 343 K until a constant sample weight was obtained. Typically, this procedure required 10 h or longer.

The soil sample was cooled to the adsorption temperature, and the 1,1,1-trichloroethane vapor was introduced into the system. The weight change of the sample resulting from the adsorption of the TCA vapor was monitored by the electrobalance and a recorder. After equilibrium was reached (typically within two hours), as indicated by a constant sample weight, the system pressure and weight of the sample were recorded. Then, more TCA vapor was introduced into the system, and the procedure was repeated for a new system pressure. Equilibrium isotherm data were collected over a pressure range of 3 mm Hg to about 90% of the saturation pressure. 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/desorption isotherm data, and the entire experimental process was repeated.
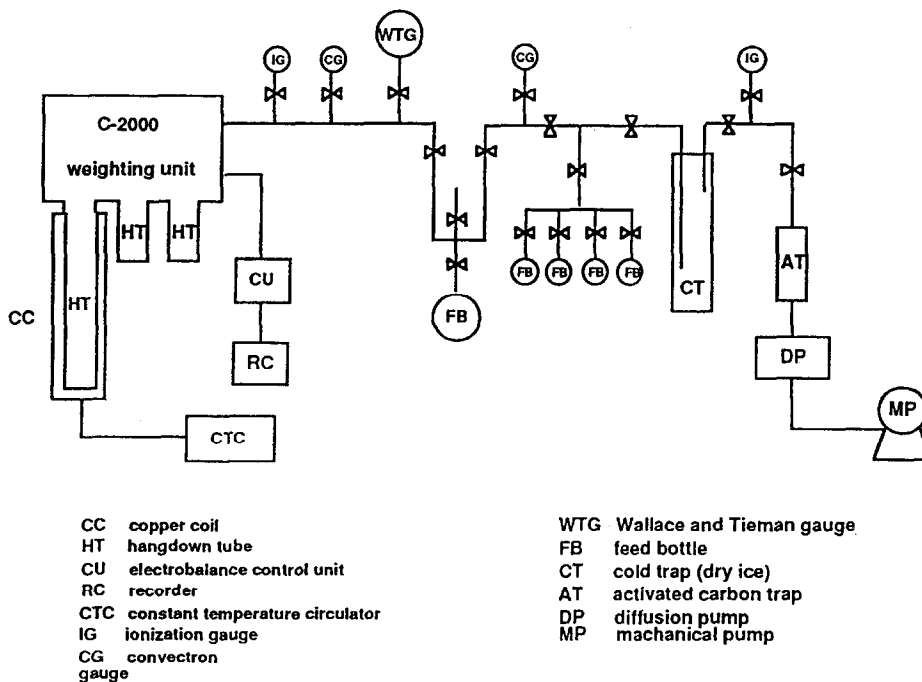

CC	copper coil	WTG	Wallace and Tiernan gauge
HT	hangdown tube	FB	feed bottle
CU	electrobalance control unit	CT	cold trap (dry ice)
RC	recorder	AT	activated carbon trap
CTC	constant temperature circulator	DP	diffusion pump
IG	ionization gauge	MP	machanical pump
CG	convectron gauge		

Fig. 3. Schematic representation of the adsorption apparatus.

3. Results and discussion

3.1. Equilibrium isotherms

Equilibrium isotherms were obtained for TCA vapor on the two test soil samples at 288, 293 and 298 K. These temperatures represent the typical dry soil temperature for the largest part of the year in several regions. The experimental equilibrium values are presented in Tables 2 and 3.

For both TCA–soil pairs examined, the isotherms were Type II according to Brunauer's classification [10], characterizing the formation of multiple layers of adsorbate molecules on the solid particle surface. Adsorption/desorption isotherms of TCA on Missouri soil at 298 K are illustrated in Fig. 4 as a typical example. These isotherms were plotted in the standard manner, namely the amount of TCA vapor adsorbed per gram of dry soil (M) as a function of the relative pressure, $P_r(= P/P_0)$, or the equilibrium pressure, P. The sharp increase of the isotherm at the larger values of the relative pressure (approximately $P_r > 0.4$) could be attributed to multilayer adsorption (i.e., induced vapor condensation) on the exterior surface of the soil sample [3]. Curvature at low relative pressure $(P_r \leq 0.4)$, referred to as the monolayer region, was scarcely visible, which could be ascribed to selective adsorption at the surface of the soil.

Considerable hysteresis effects, associated with capillary condensation, were observed upon desorption (Fig. 4 and Tables 2 and 3). As expected, the desorption curve was always above the adsorption curve. That is, more vapor was condensed from a higher pressure than from a lower pressure at a given value of P_r if a specified pressure has been approached. This could be attributed to pore geometry in that the surface curvature in contact with the vapor at a given value of P_r was different during adsorption and desorption. As pointed out by Satterfield [11] and many others, ink-bottle shaped pore structure leads to hysteresis. Accordingly, the value of P_r at which condensation occurs is determined by a larger effective radius of curvature (body of bottle), while P_r for evaporation from a filled pore is determined by a smaller effective radius of curvature (neck). Thus, the difference in the adsorption and desorption isotherms obtained in the present work was an indication of capillary condensation and an ink-bottle-type pore structure of the soils.

The reproducibility of the experimental isotherms was examined, selectively, by carrying out two consecutive adsorption/desorption cycles with the TCA vapor on soil. Several data points were reproduced within the limits of experimental error, which was no greater than 2%.

3.2. Influence of soil properties

The adsorption isotherms of TCA on two soil samples were qualitatively similar, but the equilibrium uptakes corresponding to the same equilibrium pressure were different. In Fig. 5, adsorption of TCA at 298 K by the different soil samples is compared. At other temperatures, similar behavior was observed. In all cases, the Missouri soil sample adsorbed more TCA vapor than the California soil sample. The different uptake

Table 2
Adsorption/desorption equilibrium data for 1,1,1-trichloroethane on Missouri soil

Temperature	Adsorption		Desorption	
	P (mm Hg)	M (mg/g)	P (mm Hg)	M (mg/g)
288 K	7.2	4.09	66.0	53.59
($P_0 = 77.95$ mm Hg)	14.6	6.33	60.0	37.40
	21.8	8.56	49.7	24.56
	28.2	10.42	44.6	20.47
	33.8	12.47	26.4	14.89
	39.1	14.33	14.4	9.68
	44.3	16.56	8.3	7.07
	49.0	18.98	3.2	5.21
	58.7	26.98		
	67.2	47.27		
	72.1	167.47		
293 K	5.7	3.05	80.7	44.26
($P_0 = 98.66$ mm Hg)	13.2	4.84	70.8	31.35
	20.4	6.09	60.1	23.83
	26.4	7.71	46.8	18.46
	31.8	9.32	35.0	15.23
	37.4	10.57	23.1	12.01
	42.0	12.18	13.7	6.99
	52.2	14.87	5.5	5.20
	59.3	17.74		
	67.9	21.86		
	76.0	27.95		
	83.8	37.63		
	91.1	84.39		
	93.2	154.09		
298 K	5.4	1.25	93.2	22.78
($P_0 = 123.70$ mm Hg)	12.3	2.14	79.0	17.97
	19.5	3.38	64.3	14.41
	25.9	4.27	45.2	10.68
	31.6	5.52	29.4	8.01
	37.6	6.41	17.7	4.98
	42.9	7.12	6.8	3.20
	50.8	8.36	2.9	2.31
	61.1	10.50		
	70.8	12.81		
	79.8	15.30		
	90.7	19.22		
	99.6	23.84		
	108.9	31.67		

capacities of the two soils could be attributed to both the chemical composition and the physical structure of the soil.

Because adsorption is a surface phenomenon, the surface area is of the most direct significance. The Missouri soil has a larger specific surface area than the California soil

Table 3
Adsorption/desorption equilibrium data for 1,1,1-trichloroethane on California soil

Temperature		Adsorption		Desorption	
		P (mm Hg)	M (mg/g)	P (mm Hg)	M (mg/g)
288 K	Set I	6.4	1.44	70.5	104.43
(P_0 = 77.95 mm Hg)		13.8	2.16	60.7	25.75
		20.6	3.24	53.1	16.57
		26.9	3.96	44.3	12.24
		32.7	5.22	37.5	9.90
		38.0	6.66	20.8	6.66
		43.0	7.74	10.5	4.86
		47.7	10.44	4.0	3.60
		51.9	12.42		
		55.6	13.86		
		62.0	24.67		
		67.0	46.27		
		68.9	69.68		
		71.0	249.37		
	Set II	5.8	0.71	66.7	77.09
		13.0	1.78	78.7	24.87
		19.4	3.02	50.1	15.81
		25.4	3.91	41.9	11.19
		30.6	4.97	33.8	8.35
		35.0	5.86	22.1	5.33
		39.2	7.46	10.6	3.38
		48.9	11.37	5.5	2.31
		53.8	14.92		
		58.5	19.01		
		63.8	25.93		
		70.0	206.75		
293 K	Set I	6.5	0.88	81.3	27.32
(P_0 = 98.66 mm Hg)		14.4	1.58	71.7	16.64
		21.7	2.10	54.3	9.98
		28.4	2.80	40.2	7.01
		34.8	3.68	28.3	5.43
		40.1	4.20	14.8	3.33
		46.1	5.43	4.5	2.10
		51.4	6.83		
		62.9	9.63		
		71.0	12.96		
		79.2	17.86		
		87.2	32.57		
		92.0	254.47		
	Set II	5.6	0.75	79.9	28.89
		12.8	1.86	65.3	14.35
		19.3	2.42	52.0	10.07
		24.4	3.17	39.9	7.83
		29.2	3.54	29.0	6.34
		34.3	3.91	19.8	5.03
		39.2	4.47	10.7	3.91

Table 3 (continued)

Temperature		Adsorption		Desorption	
		P (mm Hg)	M (mg/g)	P (mm Hg)	M (mg/g)
293 K	Set II	43.5	5.22	3.3	3.17
($P_0 = 98.66$ mm Hg)		52.1	6.34		
		59.9	8.02		
		66.5	9.88		
		74.8	13.99		
		82.9	22.93		
		90.6	239.14		
298 K	Set I	6.3	0.54	88.3	11.29
($P_0 = 123.70$ mm Hg)		13.2	1.26	73.4	8.42
		19.4	1.61	57.2	6.63
		25.7	2.15	35.1	5.02
		31.3	2.51	23.9	3.94
		36.1	3.05	12.4	2.87
		40.8	3.41	4.5	2.15
		45.0	3.74		
		53.9	4.48		
		63.6	5.74		
		72.8	6.99		
		80.0	8.25		
		89.9	10.40		
		101.7	14.88		
	Set II	6.6	0.73	86.5	10.36
		13.6	1.45	72.0	7.63
		20.1	1.82	64.4	6.90
		25.7	2.18	49.6	5.45
		30.7	2.54	38.2	4.72
		35.5	3.27	24.3	3.82
		40.0	3.45	11.5	2.91
		44.4	3.63	4.3	2.18
		54.8	4.54		
		63.5	5.81		
		70.0	6.54		
		78.1	7.63		
		85.0	8.72		
		95.2	12.17		
		101.7	15.26		

(Table 1). Furthermore, it has larger pore diameter and total pore volume. Therefore, the Missouri soil should have a higher adsorption capacity than the California soil does. This conclusion was supported by the entire data set (Tables 2 and 3).

For the adsorption of organic compounds by soil, the mineral content and the organic matter provide most of the surface area. The present results were in agreement with this claim. Missouri soil with 33.4% clay and 2.4% organic matter content adsorbs more than California soil with 21.7% clay and 1.7% organic matter content. It should also be noted that the percentage increases in both the clay content of the soils (33.4% from 21.7%:
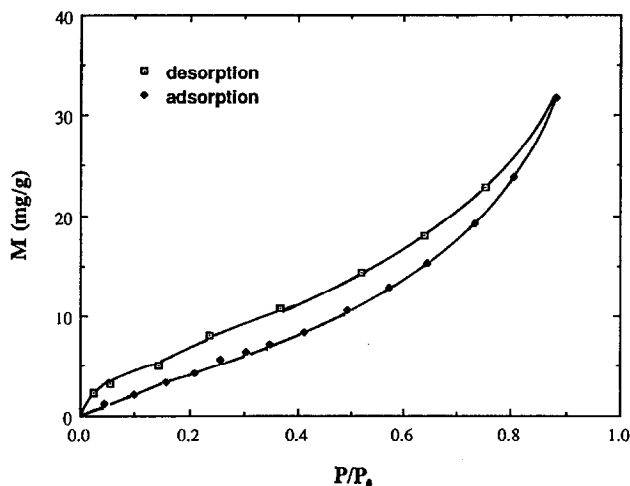
Fig. 4. Adsorption–desorption isotherms of 1,1,1-trichloroethane on Missouri soil sample at 298 K.

35% increase) and the organic matter content (2.4% from 1.7%: 41% increase) are very close to the percentage increase in their independently measured specific surface areas (44.14% from 25.33%: 42% increase). Previous investigators reported that a soil's adsorption capacity for organic compounds is primarily controlled by the organic matter in the soil under saturated conditions [2]. However, it has been postulated that, in the absence of water or under highly unsaturated conditions, the mineral matter, and consequently the clay content, dominates the adsorption of organic compounds, while the organic matter has a secondary influence on the process [9]. Because the experimental data of the present work were measured on dry soils, the greater uptake capacity of the Missouri soil may have been primarily attributable to its greater clay content.
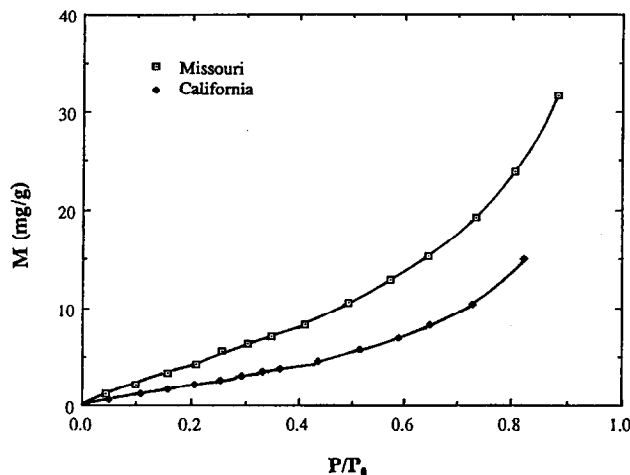
Fig. 5. Adsorption isotherms of 1,1,1-trichloroethane on Missouri and California soil samples at 298 K.

3.3. Temperature effect

Adsorption isotherms of 1,1,1-trichloroethane on California and Missouri soils were determined at 288, 293 and 298 K to investigate the influence of temperature and provide data that could be used to estimate the isosteric heat of adsorption. Vapor-phase adsorption of TCA by the soil samples was an exothermic process, which was indicated by a downward shift of the isotherms with increasing temperature. This effect is illustrated in Fig. 6 and is in agreement with the fact that the physical adsorption forces, such as Van der Waal's force, are expected to be weaker at higher temperatures. When the adsorbate vapor is condensed on the adsorbent (physical adsorption), the adsorbed molecules are loosely attached to the particle surface. Therefore, the rotational freedom of the adsorbed species is always less than that of the vapor-phase molecule; hence, the change in entropy during adsorption ($\Delta S = S_{ads} - S_{vap}$) is necessarily negative [12]. In order for significant adsorption to occur, the Gibbs free energy of adsorption (ΔG) must also be negative, which in turn requires the heat of adsorption (ΔH) to be negative because $\Delta G = \Delta H - T\Delta S$ [12]. All experimental results were consistent with the above thermodynamic principles (Tables 2 and 3).

The heat of adsorption provides a direct measure of the strength of the binding forces between the adsorbate (TCA) molecule and the adsorbent (soil) surface. In physical adsorption, the heat of adsorption generally approaches the heat of condensation of the adsorbate at higher loading. If the amount of vapor sorption is known at different temperatures, the isosteric heat of adsorption, ΔH_{ads}, can be calculated using the Clasius–Clapeyron equation:

$$\Delta H_{ads} = R[\partial \ln P / \partial (1/T)]_M.\tag{1}$$

Figs. 7 and 8 show the isosteric heats of adsorption for the two soils, plotted as a function of the amount of TCA vapor adsorbed. Such plots, commonly referred to as
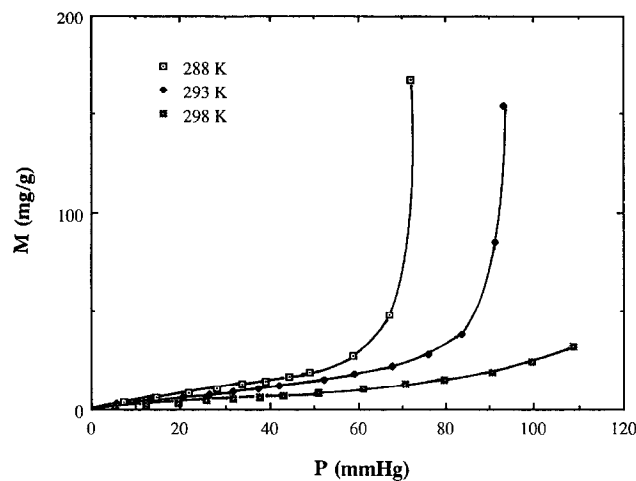

Fig. 6. Adsorption isotherms of 1,1,1-trichloroethane on Missouri soil sample at 288, 293 and 298 K.
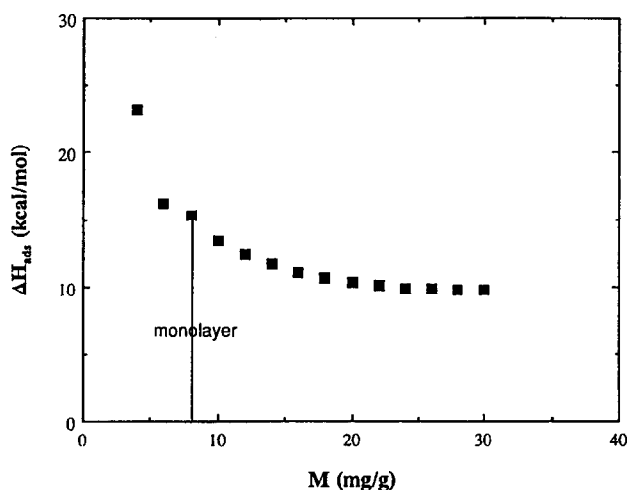
Fig. 7. Variation of isosteric heat of adsorption with increasing 1,1,1-trichloroethane adsorption on Missouri soil sample.

'heat curves', are useful in determining the thermodynamic properties of the system and in characterizing the adsorbent surface.

For an energetically uniform surface, heat curves are expected to yield a straight line with zero slope in the monolayer region, representing the heat of adsorption of the first layer. In the multilayer region, a smoothly decreasing curve usually occurs, depending upon the strength of the adsorption energy field. If the energy field is strong, the heat of adsorption of the second layer will be greater than that of the third and subsequent layers. For weak interaction forces, however, the influence of the surface on the
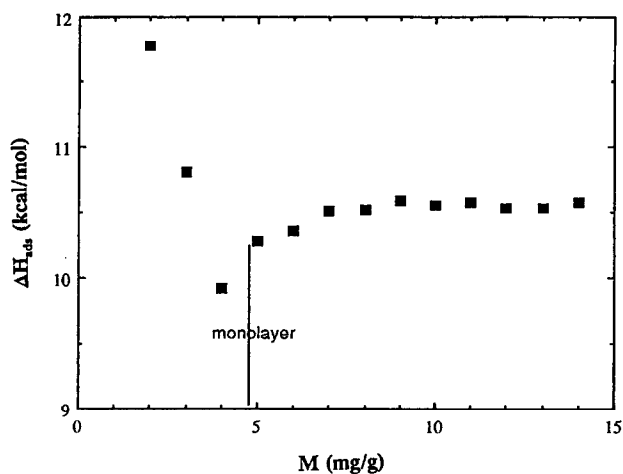

Fig. 8. Variation of isosteric heat of adsorption with increasing 1,1,1-trichloroethane adsorption on California soil sample.

multilayers will be weak. Thus, the isosteric heat of adsorption of the multilayers will be nearly constant and equal to the heat of liquefaction.

An energetically nonuniform surface, on the other hand, possesses sites with different adsorption potentials that lead to a variation in the isosteric adsorption at different loadings, even in the monolayer region. On such surfaces, adsorption initially occurs on the most active sites, giving rise to the greatest interaction energy. As these sites are filled, adsorption proceeds on the less active sites, giving off a smaller amount of heat. If the van der Waal's forces on a given occupied site are stronger than those between the adsorbate molecules and that of other unoccupied sites, higher adsorption layers can form on that particular site before the formation of the first layer is complete [13]. Consequently, a plot of isosteric heat of adsorption at different loadings usually exhibits a steep initial drop in the monolayer region, continues to decrease smoothly as the multilayers are formed, and finally levels off. Such curves are a clear indication of surface heterogeneity.

The shapes of the curves given in Figs. 7 and 8 clearly imply that the soil samples studied have energetically heterogeneous surfaces. Furthermore, the heats of adsorption shown in the figures are of the same order of magnitude as the heat of condensation of the adsorbate, which confirms that the adsorption of TCA vapor on soils is basically physical adsorption. In the monolayer region (as determined by BET analysis as shown in Table 4), the Missouri soil sample bound the adsorbate much more strongly than the California soil did (Figs. 7 and 8). This was primarily the result of its larger clay content and indicated greater energy requirements for decontamination via desorption techniques.

3.4. Data correlation

The Potential Theory of Polanyi [14] has been applied successfully for monolayer and multilayer adsorption of gases and vapors on both porous and microporous adsorbents of commercial use. However, no application regarding sorption on soils has been located in the existing literature. According to the theory, a potential field exists at the surface of the adsorbent and exerts strong, long-range attractive forces on the surrounding gas or vapor. The adsorption potential field can be divided into equipotential surfaces where the space between each equipotential surface and the solid surface corresponds to the

Table 4
Model predictions for 1,1,1-trichloroethane adsorption on soil

Soil type	T (K)	BET			GAB			
		M_m	C	Error, % ($P_r < 0.4$)	M_m	C	k	Error, % (entire set)
California	288	3.31	6.63	4.90	5.35	2.25	0.96	4.22
	293	3.19	4.40	4.98	5.87	1.58	0.94	3.36
	298	3.75	3.14	2.84	4.08	3.19	0.91	2.14
Missouri	288	8.09	8.08	1.23	7.83	10.47	0.97	2.84
	293	7.74	8.05	4.83	9.05	6.35	0.91	3.18
	298	7.66	3.104	2.02	8.61	3.41	0.85	1.46

volume adsorbed. The maximum potential appears at the adsorbent surface, while the potential decreases as the distance from the adsorbent surface increases. The adsorption potential, ϵ, which is related to the difference in free energy between the adsorbed phase and the saturated liquid sorbate at the same temperature, may be calculated directly from the ratio of the equilibrium pressure and the saturation vapor pressure:

$$\epsilon = -RT \ln(f/f_0) = -RT \ln(P/P_0) \tag{2}$$

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. It should be noted that the adsorption potential defined in this way includes both an entropy term and an energy term.

Based on the Potential Theory, 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 which is referred to as the characteristic curve. The characteristic curve provides an excellent means of summarizing equilibrium data over a wide range of temperatures. Provided that the system follows the Potential Theory, this characteristic curve can be used to forecast the seasonal (temperature-dependent) adsorption capacities of soils.

The characteristic curves of TCA on Missouri and California soil samples, plotted as cm^3 TCA adsorbed per gram of soil versus ϵ/R (i.e., $T \ln(P_0/P)$), are given in Figs. 9 and 10. As shown, the data for all temperatures were close to a single curve as predicted by the Polanyi theory. Consequently, they can be used to predict the sorption capacities at other temperatures by simple extrapolation or interpolation.

The experimental data were also correlated by BET [10,14,15] and GAB [16–18] multilayer isotherm models for future simulations. Probably the most important model for multilayer adsorption of vapors is the BET equation [10,14]. It is essentially an
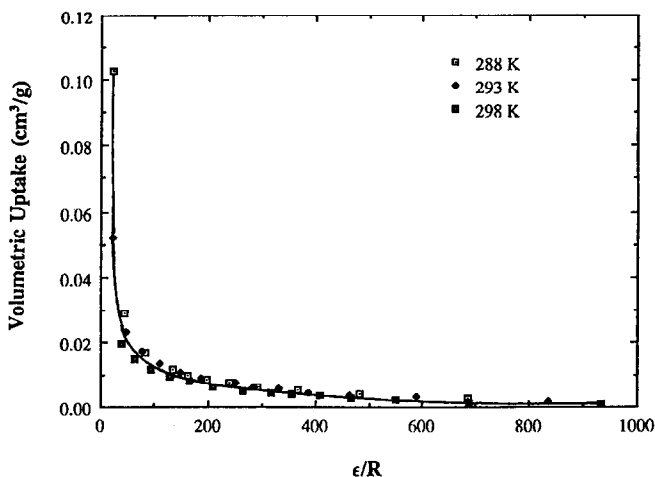

Fig. 9. Characteristic curves for 1,1,1-trichloroethane vapor on Missouri soil sample.
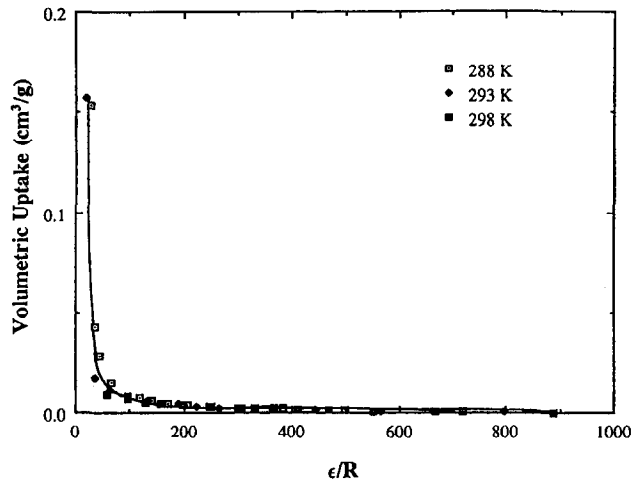
Fig. 10. Characteristic curves for 1,1,1-trichloroethane vapor on California soil sample.

extension of the Langmuir isotherm, but accounts for multilayer adsorption by assuming that each molecule in the first adsorbed layer provides one site for the second and subsequent layer. The molecules in the second and subsequent layers are considered to behave essentially as the saturated liquid, while the heat of adsorption for the first layer of molecules, which is in contact with the surface of the adsorbent, is different. The resulting equation for the BET equilibrium model is

$$\frac{P_r}{(1 - P_r)M} = \frac{1}{M_m C} + \frac{P_r(C - 1)}{M_m C},$$ (3)

where P_r is the relative pressure, M_m is the monolayer capacity, and C is a constant related to the net heat of adsorption as follows:

$$C = C_0 \exp[(q_L - q_1)/RT]; \; C_0 \approx 1.0.$$ (4)

Eq. (3) was derived based on kinetic considerations. Later it was shown that [15] it can also be derived by using statistical thermodynamics.

In independent studies, Anderson [16], De Boer [17] and Guggenheim [18] improved the BET model by assuming that the heat of adsorption of the second to approximately ninth layers differs from the heat of liquefaction by a constant amount, and that the heat of adsorption is equal to the heat of liquefaction in the layers following these. The final GAB model equation has the following form:

$$\frac{M}{M_m} = \frac{CkP_r}{(1 - kP_r)(1 - kP_r + CkP_r)},$$ (5)

where M_m and C are the same as defined in the BET equation, and the additional parameter k represents the difference between the heat of adsorption of the multilayers and the heat of liquefaction. Thus, k is a measure of the attractive force field strength and can be expressed as

$$k = k_0 \exp[(q_2 - q_1)/RT].$$ (6)

The 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 4. The best fit model parameters were obtained by using a nonlinear regression analysis. The nonlinear fit was carried out using a Fortran Package (MARQ), which performs a nonlinear least squares fit of a user-supplied function to a given set of data, using the Marquardt-S method or the Gauss–Newton method. The error percentages were calculated from the following expression:

$$\text{Abs.\% Deviation} = 100 \times \frac{(\text{experimental uptake} - \text{theoretical uptake})}{\text{experimental uptake}}. \tag{7}$$

The BET model predicted the experimental data accurately within a deviation range of 1.23% to 4.98%, for a relative pressure less than 0.4 (monolayer region). In the multilayer region, however, the average absolute percentage deviation was greatly increased (always greater than 10%) and even exceeded 100% in many cases. This could be attributed to the oversimplifying assumptions of the BET model concerning the multilayer region. On the other hand, the GAB model provided much better overall predictions than did the BET model. The average absolute percentage deviations for the entire relative pressure range were in a range varying from 1.48% to 4.22%. Model parameters for both BET and GAB equations showed no definite trend with increasing temperature.

The soil monolayer capacities (M_m) for TCA obtained from both models clearly showed that the Missouri soil sample had larger capacity. The value of M_m as determined by the GAB equation varied from 5% to 38% higher than that predicted by the BET equation. Similar results for different adsorbent/adsorbate pairs have been reported earlier, and it has been shown that the surface areas determined using the GAB monolayer values were always 5% to 10% larger than the BET areas [13,19]. However, the BET areas obtained in conjunction with a nitrogen area of 16.2 Å^2 have received so many independent experimental confirmations that the BET monolayer values for any adsorbate/adsorbent pair can be accepted as the correct values.

Using the monolayer uptake values, an attempt was made to estimate the specific surface area of the soils based on the size of the TCA molecules. The estimated surface areas based on TCA adsorption (Table 5) were 2 to 8 times less than those measured by the BET/nitrogen adsorption method (Table 1), and the discrepancy in the case of the California soil sample was greater. This was not surprising because the TCA molecule

Table 5
Specific surface areas based on 1,1,1-trichloroethane monolayer uptake

Soil type	T (K)	Surface area, m^2/g
California Soil	288	4.88
	293	4.74
	298	5.59
Missouri Soil	288	11.95
	293	11.48
	298	11.41

was much larger than the nitrogen molecule and the California soil had smaller pores. In other words, the results in Table 5 represent the surface area of each soil occupied by TCA molecules. Accordingly, a large fraction of the surface area of these test soils was unoccupied because the adsorbate molecules could not penetrate into the smaller pores.

4. Conclusions

Equilibrium adsorption–desorption data of 1,1,1-trichloroethane on dry soils were measured gravimetrically at 288, 293 and 298 K. The isotherms were of Type II and sigmoid in shape, showing considerable hysteresis between the adsorption and desorption cycles.

The distribution of major constituents of soil influences the soil's vapor sorption capacity. The results suggested that this capacity positively correlated with both the clay and the organic matter contents of the test soils. Also, a positive correlation between average pore size and sorption capacity for TCA vapor was observed.

Increasing the temperature resulted in a decrease in sorption. The values of isosteric heat of adsorption were of the same order of magnitude as the heat of liquefaction of TCA. These results confirmed that the adsorption of TCA on soil was primarily the result of physical forces. A positive correlation between the isosteric heat of adsorption of TCA and the soil's clay and organic matter contents was observed. This indicated a positive correlation between the clay and organic matter contents and the thermal energy requirement for decontamination through desorption techniques. The shape of the heat curves suggested that the soil samples were characterized by energetically heterogeneous surfaces. Thus, the removal of TCA from soil through thermal desorption will require greater specific energy (i.e., energy per unit amount of TCA removed) for the portion of TCA corresponding to the monolayer coverage, within the monolayer region, and this requirement would further increase with increasing removal efficiency.

The isotherm data were correlated by using well-known multilayer adsorption models. The results conformed satisfactorily to the Potential Theory and led to a single temperature-independent characteristic curve. The BET isotherm provided accurate correlations for relative pressures of less than 40%, while the GAB isotherm gave much better predictions than did the BET model for the higher relative pressures.

5. Nomenclature

ϵ Adsorption potential
f Fugacity
f_0 Saturation fugacity
G Gibbs free energy
H Enthalpy
ΔH_{ads} Isosteric heat of adsorption
M Equilibrium uptake
M_m Monolayer uptake

P	Equilibrium pressure
P_0	Saturation pressure
P_r	Relative pressure
q_L	Heat of Liquefaction
q_1	Heat of adsorption of the first layer
q_2	Heat of adsorption of multilayers
R	Universal gas constant
S	Entropy
T	Temperature

References

[1] K. Wolf, Pollution Prevention Rev. 2 (1993) 1.

[2] S.K. Ong and L.W. Lion, Water Res. 25 (1991) 29.

[3] C.T. Chiou, D.E. Kile and R.L. Malcolm, Environ. Sci. Tech. 22 (1988) 298.

[4] S.H. Poe, K.T. Valsaraj, L.J. Thibodeaux and C. Springer, J. Hazardous Mater. 19 (1988) 17.

[5] T.C. Chiou, P.E. Porter and D.W. Schmedding, Environ. Sci. Tech. 17 (1983) 227.

[6] J.A. Smith, C.T. Chiou, J.A. Kammer and D.E. Kile, Environ. Sci. Tech. 24 (1990) 676.

[7] J.K. Koo, D.W. Ahn, S.P. Yoon and D.H. Kim, Water, Air and Soil Pollut. 53 (1990) 267.

[8] K.T. Alben, E. Shpirt and J.H. Kaczmarczyk, Environ. Sci. Tech. 22 (1988) 22.

[9] C.T. Chiou and T.D. Shoup, Environ. Sci. Tech. 19 (1985) 1196.

[10] S. Brunauer, P.H. Emmett and E. Teller, J. Am. Chem. Soc. 60 (1938) 309.

[11] C.N. Satterfield, Heterogeneous Catalysis in Practice (McGraw Hill, New York, 1980).

[12] D.M. Ruthven, Principals of Adsorption and Adsorption Processes (John Wiley, New York, 1984).

[13] D.M. Young and A.D. Crowell, Physical Adsorption of Gases (Butterworths, London, 1962).

[14] A.L. Hines and R.N. Maddox, Mass Transfer-Fundamentals and Applications (Prentice Hall, New Jersey, 1985).

[15] T.L. Hill, Statistical Mechanics (McGraw Hill, New York, 1960).

[16] R.B. Anderson, J. Am. Chem. Soc. 68 (1946) 686.

[17] J.H. De Boer, The Dynamical Character of Adsorption (Clarendon, Oxford, 1953).

[18] E.A. Guggenheim, Applications of Statistical Mechanics (Clarendon, Oxford, 1966).

[19] A. Clark, The Theory of Adsorption (Academic, New York, 1970).