

EQUILIBRIUM VAPOR PHASE ADSORPTION OF VOLATILE ORGANIC CHEMICALS ON DRY SOILS

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(Received December 8, 1987; accepted in revised form February 15, 1988)

Summary

Equilibrium vapor phase adsorption of volatile organic chemicals (VOC) can be described adequately by the BET equation. The adsorption of five VOCs (benzene, dichloropropane, methylcyclohexane, ethyl ether and methanol) on four types of soils of moisture contents less than 2% at 30°C are reported. The adsorption of VOCs by dry soils is quite considerable and dominated by mineral adsorption. It also appears that most of the adsorption occurs on the external surface of the soils. Polar compounds show a larger degree of adsorption than non polar and slightly polar adsorbates. The high degree of adsorption observed will retard the movement of volatile organics from hazardous waste landfills and on surface soil for land application of hazardous waste when dry soil conditions exist.

Introduction

Volatile Organic Chemicals (VOCs) within a hazardous waste landfill can potentially vaporize and diffuse through the soil cap, eventually entering the atmosphere. Volatiles applied directly onto the soil surface in land treatment operations have a less restrictive pathway to the atmosphere. It has been estimated that approximately 190×10^3 Metric Tons of VOCs are emitted per year from landfills in the U.S. [1]. Thibodeaux and co-workers have proposed mathematical models to estimate emissions from landfills [2, 3] and landfarming operations [4, 5].

The mobility of VOCs through soil depends largely on the property of the chemical. The VOCs can undergo processes such as biodegradation, adsorption

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and leaching during their transport through the soil layers. Adsorption onto the soil surfaces will greatly reduce the mobility of VOCs through soil, and therefore plays an important role in determining the fate of VOCs in a landfill or landfarm. Soil moisture plays an important role in determining the extent of adsorption of neutral, non-polar molecules like most VOCs onto soil surfaces. At low moisture contents, the VOCs are strongly adsorbed to soils. The VOCs are displaced from their adsorption sites as soil moisture content increases due to competition for adsorption sites on the polar mineral surface from polar water molecules. Spencer and co-workers have investigated this phenomenon in considerable detail with regard to pesticide volatilization [6-9]. A recent review by our group showed that although a wealth of information exists on the adsorption of chemicals on moist (saturated) soils, there is an unfortunate lack of data on the adsorption of VOCs of environmental interest on dry soils [10]. Jurinak and Volman [11] studied the applicability of the classical Brauner-Emmett-Teller (BET) isotherm to describe the adsorption of ethylene dibromide, a soil fumigant on dry soil. Chiou and Shoup [12] reported experimental work on the sorption of organic vapors on dry soil and the effects of relative humidity on the sorption capacity. The markedly increased sorption of organic vapors at subsaturation humidities was attributed to adsorption on the mineral matter, which predominates over the simultaneous uptake by partition into the organic matter. Chiou and Shoup [12] showed that soil behaves as a dual sorbent in which the mineral matter functions as a conventional solid adsorbent and organic matter as a partition medium.

In order to gain further insight into the adsorption of chemical vapors of environmental interest onto dry soils, the present study focuses on the equilibrium adsorption of five typical VOCs on four different soil types and evaluating the applicability of the BET equation to represent the data. Adsorption isotherms such as reported here can be incorporated into chemodynamic models to estimate emissions of VOCs from landfills and landfarms when dry soil conditions exist.

Experimental

Experimental apparatus

An apparatus was constructed to provide various vapor phase concentrations of chemicals within a constant temperature environment. A schematic of the apparatus is shown in Fig. 1. The air stream was dried with two glass drying tubes filled with indicating Drie-Rite; the stream was then divided by a 1/4 inch (nominal) glass T-joint and each portion passed through a Matheson 602-1A rotameter type flowmeter. Both streams then entered a constant temperature oven via 1/4 inch copper tubings. One air stream was then saturated by bubbling it through two erlenmeyer flasks filled with the chemical and equipped with finely ground gas dispersion tubes. The saturated portion was

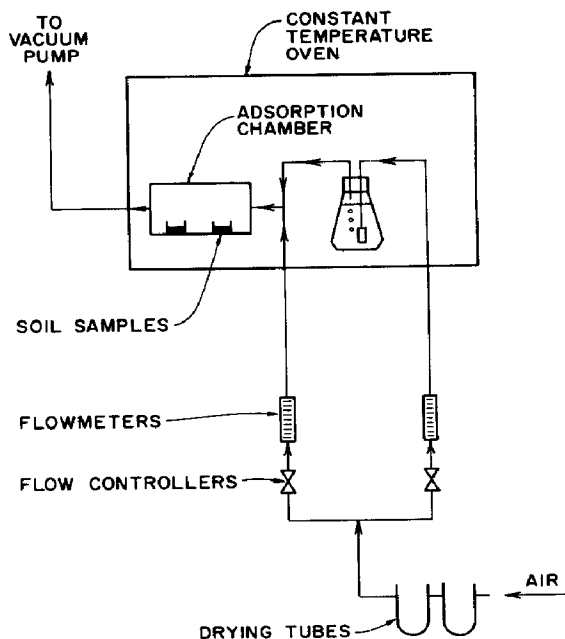


Fig. 1. Schematic of the adsorption apparatus (arrows indicate the direction of vapor and air mixture).

then rejoined with the dry-air portion and passed through an adsorption chamber containing the soil samples. A 10-liter desiccator with a ground glass lid served as the adsorption chamber. Dow-Corning High Vacuum Grease was used to seal the chamber. Stender dishes with ground glass covers were used for the soil containers. By adjusting the flow through each flowmeter various vapor concentrations were achieved within the adsorption chamber. The constant temperature oven was constructed from 1/2 inch thick polystyrene insulation. The oven dimensions were $2 \times 2 \times 1\frac{1}{2}$ ft ($0.6 \times 0.6 \times 0.45$ m). An RFL model 70 A proportional temperature controller was used in conjunction with a 100 watt light bulb to control the oven temperature at $30 \pm 1^\circ\text{C}$. A small box fan supplied continuous circulation within the oven. Flow through the system was generated with a Duo-Seal vacuum pump. Soil samples were weighed on a Sauter type 414 analytical balance.

Soil samples and chemicals

Soil samples were chosen to represent a range of physical and chemical properties. Soils were collected from the A_p horizon, 0 to 15 cm depth. Bernow soil is a fine-loamy, siliceous, thermic Glossic Palendolf, Parsons is a fine, mixed thermic Albaqualf, Summit is a fine montmorillonitic, thermic Veric Anguidoll and Weller is a fine montmorillonitic, mesic Aquic Hopludolf. The various properties are shown in Table 1. It should be pointed out that extremely dry

TABLE 1

Pertinent soil properties

Parameter/Properties	<i>Parsons</i>	<i>Summit</i>	<i>Weller</i>	<i>Bernow</i>
Texture ^a	silty loam	silty clay loam	silty clay loam	sandy loam
pH	6.0	6.6	5.2	7.2
Organic Carbon, %	0.98	2.82	0.97	0.13
CEC ^b	13.3	35.7	34.3	2.5
Sand, %	19.4	7.3	3.5	54.6
Silt, %	60.5	61.8	62.1	43.7
Clay, %	20.1	30.9	34.0	1.7
Clay mineral ^c	M-K	M	M	N/A
Moisture, % (dry basis)	1.065	0.856	1.666	0.505

^aUSDA classification.

^bCation exchange capacity, meq/cg resin.

^cM - montmorillonite, K - kaolinite, N/A - not available.

TABLE 2

Chemical properties

Compound	Molecular weight	Liquid density @ 20°C (g/ml)	Vapor pressure @ 30°C (mmHg)	Water solubility (mg/l)
Methanol	32.04	0.7961	157.55	α
Methylcyclohexane	98.19	0.7694	58.51	14
1,2-dichloropropane	112.99	1.1600	65.38	2800
Benzene	78.12	0.8790	118.0	1790
Ether	74.12	0.7077	641.8	60500

α - soluble in all proportions.

Vapor pressures were estimated using Antoine's equations [20].

samples such as used here are seldom, if ever, encountered except for the surface 1 or 2 mm in very dry climates. Covered landfills with soil this dry would seldom, if ever, be found except again in the surface 1 or 2 mm depth.

Reagent chemicals were chosen - benzene (Bz), methanol (MeOH) and methylcyclohexane (MCH) were obtained from MCB Manufacturing Chemists, Inc., 1,2-dichloropropane (DCP) was obtained from Aldrich Chemical Co., and ethylether (Et) was obtained from Fisher Scientific Company. The relevant properties are given in Table 2. The chemicals were so chosen as to represent a range of aqueous solubilities, vapor pressures and molecular weights. Benzene is the least polar while methanol is the most polar of the five compounds. Benzene has been found to be a landfill gas in many instances.

Experimental procedure

Soils were ground to pass through a standard 60-mesh ($< 250 \mu\text{m}$) screen and dried at 60°C for 24 h. After drying the soil samples were placed in a desiccator filled with Drie-Rite for 2 weeks. Drying at 60°C was preferred over drying at 105°C so as not to affect the soil's organic matter composition. The residual moisture contents for soils were measured by determining the loss of weight on drying at 105°C for 24 h. The residual moisture content for soils are given in Table 1.

Samples of approximately 1 to 3 grams were spread out in glass containers and placed in adsorption chambers. Two replicate samples of each soil were used along with one empty container as a control sample. Relative flow rates of dry air and saturated air streams were adjusted for the desired concentration within the adsorption chamber. Total flow varied from 10–50 cm^3/min . After 24 h, ground glass lids were placed on the soil and control containers, the soils removed from the adsorption chamber and weighed for uptake of VOCs. This was repeated every 24 h until sample weights remained constant. The difference in weight was taken to be the uptake of VOCs by soils at equilibrium. Any increase in weight for the control containers was subtracted so as to account for adsorption on the glass containers. These experiments were repeated for various vapor concentrations by increasing or decreasing the dry air flow rate into the adsorption chamber. When adsorption measurements were completed for a particular chemical, the entire system was purged with dry air for 24 h.

Vapor samples from the exhaust line were collected in a Pressure-Lok syringe (10 μl capacity) and analyzed on a Hewlett Packard 5890 Gas Chromatograph equipped with a Flame Ionization detector. A 6 ft \times 1/8 inch stainless steel column packed with Chromosorb 102 was used. Helium was the carrier gas. The oven, detector and injector temperatures were 190°C , 210°C and 220°C respectively. The chromatographic peaks were stored and integrated on a HP3392A Integrator.

BET equation

Brauner, Emmett and Teller [13] first proposed a comprehensive theory for multimolecular layer adsorption of organic vapors on solid surfaces. The general equation derived for the purpose is:

$$\frac{W}{W_m} = \frac{XC}{(1-X)} \left\{ \frac{1 - (n+1)X^n + nX^{n+1}}{1 + (C-1)X - CX^{n+1}} \right\} \quad (1)$$

where W is the amount of vapor adsorbed per gram of solid at pressure p , W_m is the monolayer adsorption capacity, $X = p/p_s$ where p_s is the saturation pressure, C is related to the heat of adsorption and heat of liquefaction of the vapor and n is the number of adsorbed layers existing on the surface.

Equation (1) has two limiting cases. For adsorption on a free surface as $n \rightarrow \infty$, the equation reduces to

$$\frac{X}{W(1-X)} = \frac{1}{W_m C} + \frac{(C-1)X}{W_m C} \quad (2)$$

On the other hand when adsorption is limited to a monolayer, i.e., $n = 1$, eqn. (1) reduces to a modified Langmuir isotherm,

$$X/W = 1/CW_m + X/W_m \quad (3)$$

The generalized BET isotherm (eqn. (1)) describes all the five different types of isotherms most often encountered in the adsorption of vapors on solid surfaces. Comprehensive discussions of Types I-V BET isotherms are given in the classic books by Adamson [14] and Brauner [22]. As shown by eqns. (1)-(3), the value of n is an important parameter in determining the shape of the isotherm. The BET theory, however does not provide physical interpretation as to which property of the system restricts adsorption to n -layers. Capillary pores certainly would have a limiting effect, and hence, several investigators have used the n values to characterize the average size of capillaries involved in the adsorption process [21, 22]. In spite of its shortcomings, the BET equation has been used to represent adsorption of various vapors on a variety of solids with considerable success [14, 22]. In relation to eqn. (1), Joyner et al. [21] proposed a method to determine n , W_m and C by rewriting eqn. (1) as

$$F/W = 1/W_m C + Y/W_m \quad (4)$$

where

$$F = X\{1 - X^n - X^n(1 - X)\}/(1 - X)^2 \quad (5)$$

and

$$Y = X\{1 - X^n\}/1 - X \quad (6)$$

The data should yield a straight line when F/W is plotted against Y . From the slopes and intercepts one can obtain W_m and C . Appropriate values of n should be chosen as to obtain the best possible fit of experimental data over the entire range of relative pressures studied. Equations (1) and (4) can be used to fit the experimental data using the three constants n , W_m and C . The BET equation gives values of the monolayer capacity for Type II or sigmoid shaped isotherms. The value of C is related to the net molar heat of adsorption in the first layer, E_1 , by the equation

$$(E_1 - L) = RT \ln C \quad (7)$$

where L is the molar heat of liquefaction of the vapor [12]. Jurinak and Vol-

man [11] and Chiou and Shoup [12] have shown the appropriateness of the BET equation for describing the adsorption of a variety of organic vapors on dry soils. As discussed in detail by Jurinak and Volman [11], the use of the three parameters n , W_m and C should allow meaningful comparisons to be made of the interaction of chemical vapors on soil systems.

Results and discussion

The amount of VOCs adsorbed is expressed as weight of chemical per gram of dry soil. The vapor phase concentration is determined by taking the average chromatographic peak area and converting it to a vapor density from a previously generated standard curve. Relative pressure ($X=p/p_s$) is obtained by dividing the vapor density by the pure component vapor density.

A linear fit to eqn. (4) was used to obtain the values of W_m and C from the raw adsorption data. Successive values of n were chosen until the best curve was obtained over the entire range of relative pressures. Table 3 gives the results of these calculations. In it are indicated the values of n for the best curve fit, the range of relative pressures over which the data was fitted and the correlation coefficient for the best fit. This is the same procedure used by Jurinak and Volman [11] in describing their adsorption data of ethylene dibromide on dry soils. The solid lines in Figs. 2-5 were calculated using these values of n , W_m and C in eqn. (1). Because of the low adsorptive capacity for Bernow soil and consequent scatter in experimental data, usually little correlation existed between model and measured data for this soil. The same was true for those other cases of low adsorption (e.g. benzene on Summit soil).

In Figs. 2-6 are shown the values of adsorbed concentrations of the two replicate samples as the upper and lower ends of the vertical lines along with the average value. Only the average values were used in obtaining the values of n , W_m and C . It should be noted that even though only duplicate samples were used in these experiments, the degree of agreement between the two samples was good.

Figures 2-6 represent the adsorption of the five VOCs on the four different soils studied at room temperature. Notice that the isotherms are all non linear in sharp contrast to adsorption isotherms for the compounds from aqueous systems. The isotherms for the compounds on dry soil show Type II and Type III of the BET isotherms in the case of ether, benzene, methanol and dichloropropane. The methylcyclohexane data show Type I and Type II BET isotherm characteristics. It is apparent from Figs. 2-5 that multimolecular layer adsorption occurs for vapors on dry soils. A large amount of each VOC is adsorbed on all the soils. The isotherms for ether show clear Type II BET isotherm behavior for all soils (Fig. 2). Notice the points of inflection at low X , followed by a near linear region; at high X values the curves inflect upward. whether these curves would go through $X=1$ could not be determined because of the inability in these experiments to reach more than 90% saturation of

TABLE 3

BET constant for various chemical and soils

Soil type	<i>n</i>	<i>C</i>	<i>X_m</i> (mg/g)	Range of <i>X</i> for Data fit	Correlation coefficient
<i>Chemical: ethyl ether</i>					
Weller	12	35	8.4	0.10-0.90	0.9982
Summit	8	27	4.6		0.9980
Parsons	8	29	5.2		0.9984
Bernow	7	30	1.3		0.9939
<i>Chemical: benzene</i>					
Weller	4	20	11.3	0.10-0.50	0.9986
Summit	5	3	6.0		0.9123
Parsons	15	2	7.3		0.9090
Bernow			No correlation		
<i>Chemical: methanol</i>					
Weller	4	23	18.9	0.13-0.78	0.9818
Summit	8	43	8.6		0.9897
Parsons	6	46	10.4		0.9882
Bernow			No correlation		
<i>Chemical: dichloropropane</i>					
Weller	4	32	12.7	0.06-0.57	0.9970
Summit	26	8	9.2		0.9922
Parsons	6	8	8.2		0.9715
Bernow	10	18	1.2		0.9237
<i>Chemical: methylcyclohexane</i>					
Weller	4	12	9.5	0.05-0.48 0.05-0.63	0.9720
Summit	1	98	6.5		0.9841
Parsons	1	71	8.5		0.9715
Bernow	1	177	2.0		0.9916

vapor. The saturation levels achieved for the chemicals were: ether 90%, methanol 70%, benzene 50%, MCH 62%, and DCP 57%.

As indicated in Fig. 3 benzene adsorption on Weller soil display the beginnings of sigmoid shape while benzene adsorption on Summit and Parsons soils show Type III isotherms. Methanol and dichloropropane on Weller, Parsons and Summit soils show the beginnings of Type II isotherms (Figs. 4 and 5). However for methylcyclohexane the isotherm more closely resembles a Type I (Langmuir) for Summit and Parsons soils and Type II for Weller soil.

Weller soil shows the largest uptake for all the chemicals while Bernow soil shows the smallest adsorption. Generally the data follow the trend of increasing adsorption capacity as: Weller \gg Summit \cong Parsons \gg Bernow. This is not unexpected since Weller soil has the largest clay content and surface area while Bernow has the least clay content and the smallest surface area.

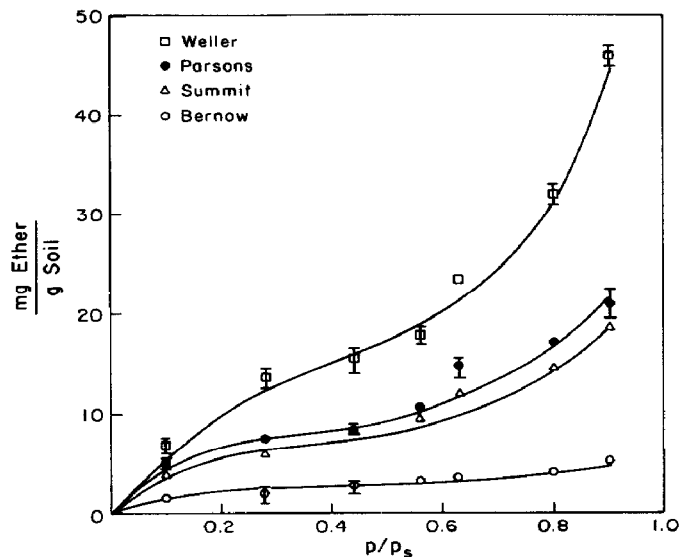


Fig. 2. Adsorption isotherms for ethyl ether.

It is also apparent that certain general tendencies for adsorption potential for each compound exists. For example, the extent of adsorption on all soils was greatest for methanol and least for benzene. Although the following order was not always observed, it was generally: methanol \gg dichloropropane $>$ methylcyclohexane \cong ethyl ether $>$ benzene. It is interesting to note that methanol is the most polar of the compounds investigated in this study. The conclusion may thus be drawn that in the case of dry soils, the extent of sorption will be largest for polar compounds. The same conclusion was drawn by Chiou and Shoup [12] from their work on adsorption of a series of chlorobenzenes on dry Woodburn soil.

It has been shown previously by Chiou and Shoup [12] that for dry soils, the role of mineral matter predominates over organic matter in adsorption of neutral molecules. This fact is confirmed by the present results. For example, even though Summit soil has a 2.82% organic matter content and Weller soil has only a 0.97% organic matter content, the latter adsorbs more than the former. On the other hand, Summit soil has only 30.9% clay content while Weller soil has a 34% clay content. Similarly even though both Weller and Parsons soils have the same organic carbon content, Weller with 34% clay content adsorbs far more than Parsons with only 20% clay content.

The values of C fell within the range 2 to 177. These values are in line with those found in previous work on dry soil adsorption of other compounds [11, 12]. The monolayer capacities W_m show clearly that Weller soil has the largest capacity while Bernow soil has the least. The values of C show large variations between 2 to 177. However, as expected low values of C are obtained for Type III isotherms, large values for Type I isotherms and intermediate values for

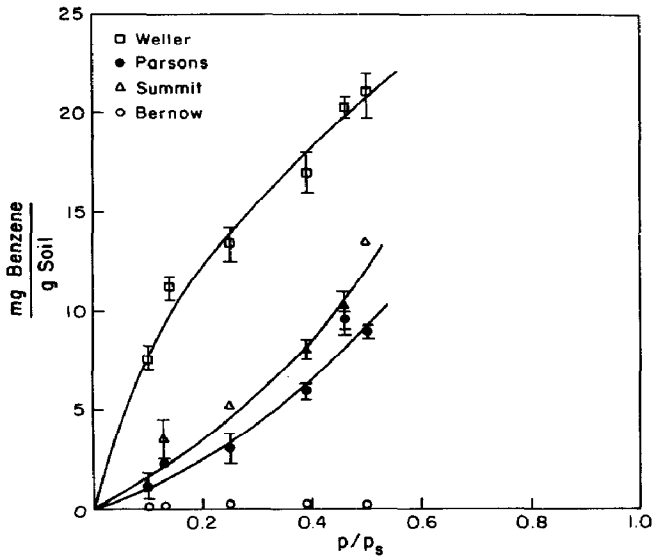


Fig. 3. Adsorption isotherms for benzene.

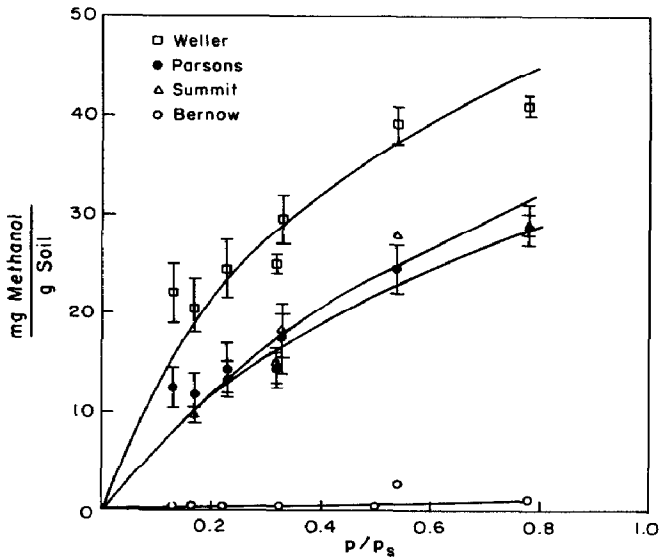


Fig. 4. Adsorption isotherms for methanol.

Type II isotherms [14]. The value of C only affects the knee of the BET isotherm at low X values [15]. There does not seem to be a specific relationship between the constant C and soil type. Adsorption parameter C depends very much on the chemical adsorbate. As discussed by Jaycock and Parfitt [15] since the isotherm shape depends more on W_m for C values larger than 10, accuracy in specifying C is less important as far as the isotherm shape is concerned.

As indicated by eqn. (7) the value of C gives an estimate of the molar heat of adsorption of molecules in the first layer given by E_1 . These values are given

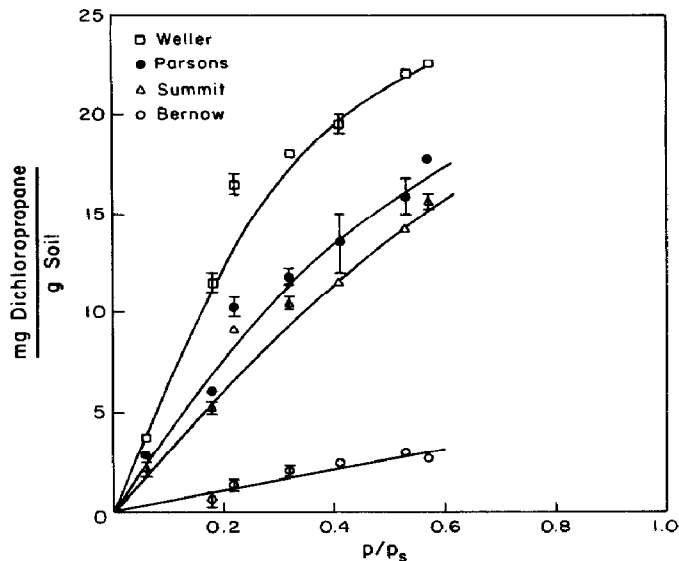


Fig. 5. Adsorption isotherms for 1,2-dichloropropane.

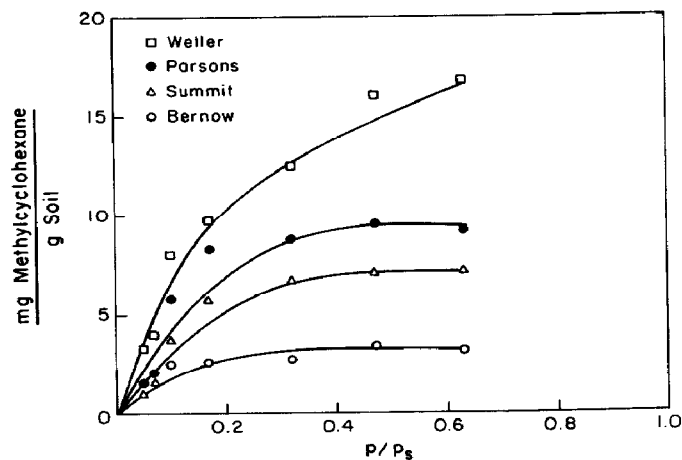


Fig. 6. Adsorption isotherms for methylcyclohexane.

in Table 4. The $E_{1,}$ values in all these cases are more exothermic than the respective L values by about 1–2 kcal/mol which is consistent with the dominance of mineral adsorption for dry soils as was shown previously by Chiou and Shoup [12] and Jurinak and Volman [11].

The monolayer capacity W_m can be related to the specific surface area of the soil S (m^2/g) using the simple equation

$$W_m = SM/NA_m \quad (8)$$

where A_m is the projected area of a molecule in the monolayer, M is its molec-

TABLE 4

Molar heats of adsorption for VOCs on soils

Soil type	Molar heat of adsorption, E_1 , (kcal/mol)	Molar heat of condensation, L , (kcal/mol) - Ref. 19
<i>Chemical: ether</i>		
Weller	8.5	6.4
Summit	8.3	
Parsons	8.3	
Bernow	8.4	
<i>Chemical: benzene</i>		
Weller	9.1	7.4
Parsons	7.8	
<i>Chemical: methanol</i>		
Weller	10.0	8.2
Summit	10.4	
Parsons	10.5	
<i>Chemical: dichloropropane</i>		
Weller	9.6	7.6
Summit	8.8	
Parsons	8.8	
Bernow	9.3	
<i>Chemical: methylcyclohexane</i>		
Weller	8.8	7.4
Summit	10.1	
Parsons	9.9	
Bernow	10.4	

ular weight and N is the Avogadro's number. Following the suggestion of Emmett and Brauner [16] A_m can be calculated using the equation

$$A_m = f (M/dN)^{2/3} \quad (9)$$

where f is the packing factor (usually 1.091 for hexagonal close packing) and d is the density of the adsorbed molecule. The value of A_m is greatly variable because of several factors such as the nature of adsorbent, lateral interactions between adsorbed molecules, variation in distance between adsorbing sites, etc. Thus, reasonable care must be exercised in drawing conclusions from the value of S calculated in this way. The results are shown in Table 5. Also shown are the total surface areas of the soils calculated using the areas of the various constituents of the soil tabulated by Fuller [17] and Bailey and White [23]. The results show that the S values calculated from W_m determinations are all reasonably close for each soil except for the methanol-based calculations. The methanol-based values are approximately three times those predicted on the basis of the other four compounds. This may be due to the fact that montmo-

TABLE 5

Apparent soil surface area

Compound adsorbed	Soil surface area (m ² /g)			
	Bernow	Parsons	Summit	Weller
Ether	4	13	13	24
MCH	5	13	10	22
Benzene	—	15	—	26
DCP	2	15	13	19
MeOH	—	38	42	62
Total area*	14	168	270	280

*Calculated using values of total areas of individual soil constituents given by Fuller [16] and Bailey and White [23].

rillonite clays wetted by polar liquids or vapors, undergo interlayer expansion and hence expose a large internal surface area which normally would not be available for adsorption of a non-polar or a slightly polar molecule [18]. Discounting the methanol data, it appears that the monolayer capacities may be

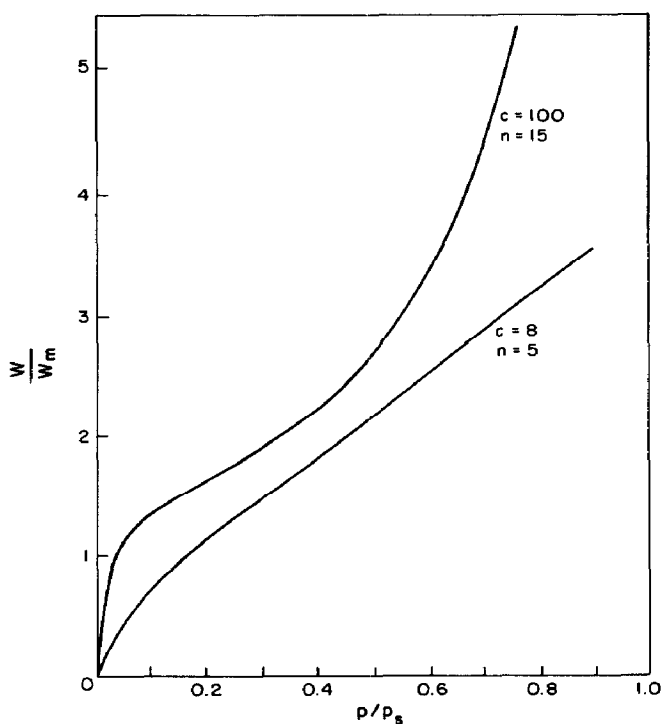


Fig. 7. Combined influence of constants C and n on BET equations for the adsorption of VOCs on dry soils.

successfully used to obtain the apparent soil surface areas for the BET adsorption isotherms of non-polar molecules on dry soils.

Jurinak and Volman [11] compared the measured total surface areas of four dry soils using the ethylene glycol retention method with those calculated from the monolayer capacities of ethylene dibromide using this procedure. They concluded that the area thus calculated correlated well with the external surface area of the soil, while the internal surface area was largely unavailable for adsorption. The same trend is displayed in Table 5 where the calculated total surface areas are much larger than the values calculated from the monolayer capacities. It thus appears that for non-polar and slightly polar compounds only the external surface area is available for adsorption.

It should be mentioned that even though we observed no specific relationship between the organic matter content and adsorption because of the predominance of adsorption by mineral matter, the influence exerted by organic matter in adsorption by blocking adsorption sites on dry clays cannot be completely ruled out. It is fairly well known that organic matter coatings occur on clay surfaces. If adsorption were only related to clay content and surface area, Summit and Weller soils should show about the same degree of VOC adsorption. However, Summit has a larger organic matter content than Weller (2.82 vs. 0.97) suggesting the possibility of adsorption site blockage. So more experiments are required to throw light on this aspect of adsorption.

Figure 7 shows the combined effects of the constants C and n on the BET equation, i.e. eqn. (1). Most of the data in this study fell within the area bounded by the two curves. Therefore, with accurate estimates of W_m and average values of C and n , one can obtain an order of magnitude estimates of the equilibrium adsorption of VOCs by common dry soils. It may be instructive in further work to study the desorption process as well, as soils invariably display adsorption-desorption hysteresis. Since in the field one usually finds a large number of VOCs as multi-component systems, further study of such systems to elucidate interactions among adsorbed molecules should also be considered.

Conclusions

We conclude that the present equilibrium adsorption method yields reasonably accurate data except for the cases of specific soil/compound interactions that result in very low adsorbing capacities (due to the experimental error in weighing). Furthermore, the BET model can be used to adequately describe equilibrium vapor phase adsorption of VOCs by dry soils over a wide range of pressures.

Based on our observations, coupled with those of Jurinak and Volman [11] and Chiou and Shoup [12], we conclude that in the case of adsorption of VOCs by dry soils, organic matter has little influence on adsorption, that adsorption is dominated by mineral content and that adsorption is mostly limited to the

external surface of the dry soil. It appears that the molecular polarity of the adsorbate plays an important role in adsorption. Also, interlayer swelling of montmorillonite can occur when polar molecules are being adsorbed by dry soils, especially those with hydrogen bonding potential, and thus causing an increase in adsorption.

ACKNOWLEDGEMENTS

We thank Dr. Duane C. Wolf, Department of Agronomy and Soil Science, University of Arkansas, Fayetteville for providing us the soil samples used in this study. This paper was presented at the 194th National Meeting of the American Chemical Society at New Orleans, LA on Sept. 31–Oct. 4, 1987. We thank two anonymous reviewers for several helpful comments.

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