

# A prediction method for gas-phase VOC isotherms onto soils and soil constituents

J.F. Campagnolo, A. Akgerman \*

*Chemical Engineering Department, Texas A&M University, College Station, TX 77843-3122, USA*

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## Abstract

Similarities in the adsorption isotherms of various non-polar volatile organic chemicals (VOCs) on dry soils and clay minerals are used to develop an empirical predictive method to estimate the isotherm parameters of the BDDT (three-parameter BET) model. Single-component adsorption data of nine VOCs on both soils and clay minerals and also nitrogen adsorption are examined. The familiar practice of reducing isotherms by the BET monolayer coverage is applied, and it is shown that isotherms of different VOCs on the same adsorbent collapse into a single isotherm. A simple prediction method based on this observation is presented.

*Keywords:* Adsorption isotherm; Soil; Volatile organic chemical

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## 1. Introduction

The interest in gas-phase adsorption of volatile organic chemicals (VOCs) by soils and soil constituents, such as clay minerals, arises from a number of sources. In addition to interest in engineered clays as a commercial adsorbent, there is also the recognition in environmental science that direct gas-phase adsorption to the soil surface plays a role in the atmospheric and subsurface transport of VOCs in soils [1,2].

A small number of studies have been conducted for single-component VOC adsorption onto dry soils. In reviewing the literature on the subject, Valsaraj and Thibodeaux [3,4] have reported that under dry conditions (soil moisture content below 2%) VOC adsorption usually displays the characteristic Type II and Type IV BET isotherms. Under these conditions the single-component BET model adequately describes sorption

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\* Corresponding author. Tel. and Fax: 409-845-3375; E-mail: a0a9742@chennov1.tamu.edu.

behavior. Generally, the conclusions to be drawn from VOC adsorption studies for non-polar and slightly polar VOCs onto soils are: (i) adsorption by soils is essentially an external surface phenomenon limited mostly to clay mineral surfaces [5–7]; (ii) differences in the adsorptive potential of soils is primarily a manifestation of differences in external surface areas [5]; (iii) adsorption of VOCs increases with increasing adsorbate polarity [6,7]; and (iv) the same intraparticle surfaces inaccessible to  $N_2$  when used as an adsorbent are inaccessible to VOCs [5,8].

Single-component VOC adsorption on dry constituents of soil has also received some attention. Under a dry condition or one of very low humidity, the behavior of clay minerals and soils is very similar, as the former are the predominant adsorbents in soils at zero humidity. The conclusion of Jurinak and Volman [5] with regard to external surface area measurements with ethylene dibromide (EDB) were essentially the same as those drawn by Jurinak [9] for the sorption of EDB on clays (kaolinite, illite and montmorillonite) possessing different exchangeable cations. Jurinak also determined that the nature of the exchangeable cation had some effect on adsorption. Similarly, Rhue et al. [8] reached the same conclusions for the clay minerals they included in their experiments. Ong and Lion [10] performed vapor sorption experiments for trichloroethylene (TCE) on dry soil constituents which included clays (montmorillonite and kaolinite) among other inorganic and organic substances. They found that BET surface areas computed from TCE adsorption were lower than those estimated by the  $N_2$ /BET method for all solids. Assuming that the  $N_2$ /BET values were correct, they computed what the molecular cross-sectional areas of TCE should be to make up those surface areas, an approach taken by Van Voorhis et al. [11]. The computed areas were 1.5–2 times the theoretical values obtained from the close hexagonal packing model. Similarly, Campagnolo and Akgerman [12], after examining the adsorption of *n*-hexane on a number of soil constituents including five clay minerals (kaolinite, two smectites, bentonite, and illite), found that the BET surface areas of the clay minerals obtained from *n*-hexane adsorption measurements at 27°C were consistently  $\approx 0.73$  times the BET surface areas obtained by the standard nitrogen technique.

In the presentation and comparison of sorption data, results are sometimes expressed as a relative isotherm (adsorption capacity divided by BET-estimated monolayer capacity). This has the effect of eliminating the surface area bias and making sorbent-specific interactions more apparent [9,10]. Others have reported isotherms in this manner [5,8,13]. Pennell and Rao [14] and Campagnolo and Akgerman [12] have expressed isotherms relative to  $N_2$ /BET surface area.

Recently, Goss [2] has developed a method for prediction of isotherms for very low levels of the VOCs in the gas phase adsorbing onto polar mineral surfaces, where the adsorption isotherm is approximately linear. Additionally, Kreamer et al. [15] have fitted VOC gas-phase adsorption data (where quartz was the solid) to a Freundlich model in which the estimates of the exponent obtained were approximately unity. However, again, at higher gas-phase concentrations the linear assumption usually fails, as the isotherms display a BET Type II sigmoid shape.

The purpose of this study was to investigate the vapor-phase, single-component adsorption of VOCs onto soils and clay minerals. Conventional nitrogen adsorption experiments were also performed on the same samples to determine whether there was

any correlation between the two classes of adsorbates. The objective was to develop a method of predicting adsorption isotherms for VOCs on natural adsorbents by use of similarities found in the experimental isotherms of nitrogen and the VOCs when plotted in terms of the reduced concentrations. The method is empirical and based within the theoretical framework of the BET equation.

## 2. Materials and methods

A summary of the adsorbents and adsorbates used in the experiments is given in Tables 1–3. We used a static adsorption technique in determining the adsorption isotherm, employing a Micromeritics Accusorb 2100-E. The dry soils were placed in the adsorption chamber and degassed to  $< 10^{-3}$  Torr for a period of 10–12 h at a temperature of approximately 130°C, after which the adsorption chamber was brought to 27°C. All experiments were operated at 27°C. The VOC vapor was introduced into the gas chamber via a manifold and, upon equilibration, the pressure was recorded. The vapor was then allowed to expand into the adsorption chamber by opening the sample port valve. When the system had again equilibrated, the final pressure was recorded. As the volume and temperature of the manifold, intermediate piping and flask void space were known, the number of initial and final moles of vapor was computable via the perfect gas law. The quantity adsorbed was estimated from the Accusorb data by computing the difference in moles of vapor from the initial to the final state. The

Table 1  
Characteristics of some soils used in the experiments

Adsorbent	Mineralogy	Composition	Particle size ( $\mu\text{m}$ )
Soils			
Highbanks A	Smectite, illite	58.6% clay	< 2
		37.5% silt 3.9% sand (1.0% organic C)	$2 < D_p < 50$ > 50
Highbanks B	Smectite, illite	25.6% clay	< 2
		51.8% silt 22.6% sand (0.7% organic C)	$2 < D_p < 50$ > 50
Reagan A	Illite, smectite, kaolinite	34.2% clay	< 2
		51.2% silt 14.6% sand (2.3% organic C)	$2 < D_p < 50$ > 50
Reagan B	Illite, smectite, kaolinite	32.4% clay	< 2
		52.0% silt 15.6% sand (3.9% organic C)	$2 < D_p < 50$ > 50

Table 2  
Characteristics of clay minerals used in the experiments

Adsorbent (clay mineralogy)	Particle size ( $\mu\text{m}$ )	Charge per formula unit ( $\text{mol e}^-$ per unit)	Composition
Bentonite (smectite)	< 44	0.2–0.6	$\approx$ 93% clay; $\approx$ 7% oxides/salts of Ca, Fe, other
Illite (mica)	< 210	0.6–0.9	$\approx$ 90% clay; $\approx$ 10% quartz and other
Kaolin (kaolinite)	0.1–4	0.0	$\approx$ 98% clay; $\approx$ 2% oxides/salts of Na, Fe
Na montmorillonite (smectite)	0.5–1	0.2–0.6	$\approx$ 90% clay (incl. montmorillonite, some feldspar, mica); $\approx$ 10% silicates of Na and Fe, quartz, nitrates/carbonates of Fe
Mg montmorillonite	< 4	0.2–0.6	$\approx$ 99% clay

adsorption isotherm was obtained by repetition of the process at gradually higher manifold pressures.

The piping and manifold of the Accusorb are constructed from polished Monel. Wall effects on adsorption were estimated by evacuating the system after attaching an empty flask to an open sample port, then introducing hexane until the system pressure was 149.5 mmHg and recording the pressure response over 18 h. The final pressure after this time was 149.0 mmHg. The leak rate of air into the evacuated system was previously determined to be  $\approx 10^{-4}$  mmHg  $\text{min}^{-1}$ , so that the maximum wall adsorption of hexane over the time period was estimated to be  $\approx 0.1$  mg hexane. The wall adsorption was considered to be negligible and not considered in reducing the adsorbent experimental data. The details of the experimental technique are explained elsewhere [12].

Table 3  
Properties and purities of adsorbates

Adsorbate (Formula)	Purity (%)	Molec. Wt. ( $\text{g mol}^{-1}$ )	$\rho_{\text{LIQ}} _{300\text{ K}}$ ( $\text{g ml}^{-1}$ )	Dipole (Debye)	$P_0 _{300\text{ K}}$ (mm Hg)
Methylene Chloride ( $\text{CH}_2\text{Cl}_2$ )	99.9	84.9	1.31	1.8	459.1
Chloroform ( $\text{CHCl}_3$ )	99.8	119.4	1.47	1.1	211.0
Carbon Tetrachloride ( $\text{CCl}_4$ )	99.9	153.8	1.58	0.0	126.0
Benzene ( $\text{C}_6\text{H}_6$ )	99.9	78.1	0.87	0.0	104.0
Toluene ( $\text{C}_7\text{H}_8$ )	99+	92.1	0.86	0.4	32.6
Pentane ( $\text{C}_5\text{H}_{12}$ )	99.3+	72.2	0.61	0.0	571.0
Hexane ( $\text{C}_6\text{H}_{14}$ )	99+	86.2	0.64	0.0	170.0
Heptane ( $\text{C}_7\text{H}_{16}$ )	99+	100.2	0.67	0.0	51.0
Methanol ( $\text{CH}_3\text{OH}$ )	99.9	32.0	0.79	1.7	141.0

### 3. Data and analysis

#### 3.1. Theory

According to the BET theory of Brunauer et al. [16], multilayer adsorption onto an adsorbent can be represented by the linear equation

$$\frac{y}{X(1-y)} = \left( \frac{C_{\text{BET}} - 1}{X_m C_{\text{BET}}} \right) y + \frac{1}{X_m C_{\text{BET}}} \quad (1)$$

where  $X_m$  is the amount adsorbed corresponding to monolayer surface coverage and the parameter  $C_{\text{BET}}$  is related to the net heats of adsorption and of vaporization by

$$-\ln C_{\text{BET}} \approx \frac{(\Delta H_m + \Delta H_v)}{R_g T} \quad (2)$$

where  $\Delta H_m$ , the heat of adsorption, is normally a negative quantity, because it is heat released. For Type II isotherm data, Eq. (1) is typically applicable over the range  $y = P/P_0$  from 0.05 to 0.30. Adsorption isotherm data can then be fitted by least-squares linear regression analysis to yield estimates of the two parameters  $X_m$  and  $C_{\text{BET}}$ .

The projected area of a single adsorbate molecule can be computed by the hexagonal close-packing model, which assumes spherical molecules

$$\alpha_m = 1.091 \left( \frac{M}{N_0 \rho} \right)^{2/3} \quad (3)$$

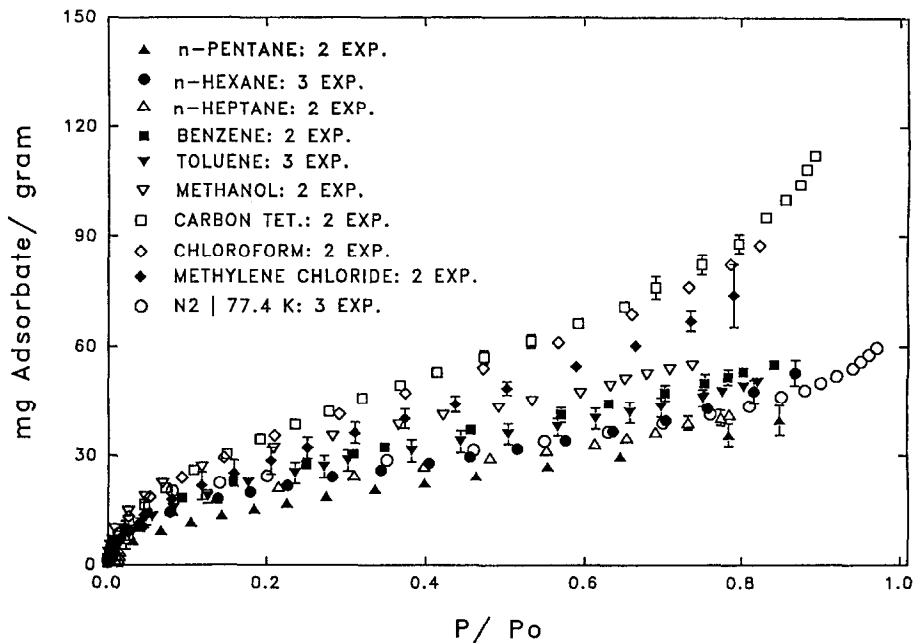


Fig. 1. Adsorption isotherms of various VOCs on Highbanks A soil.

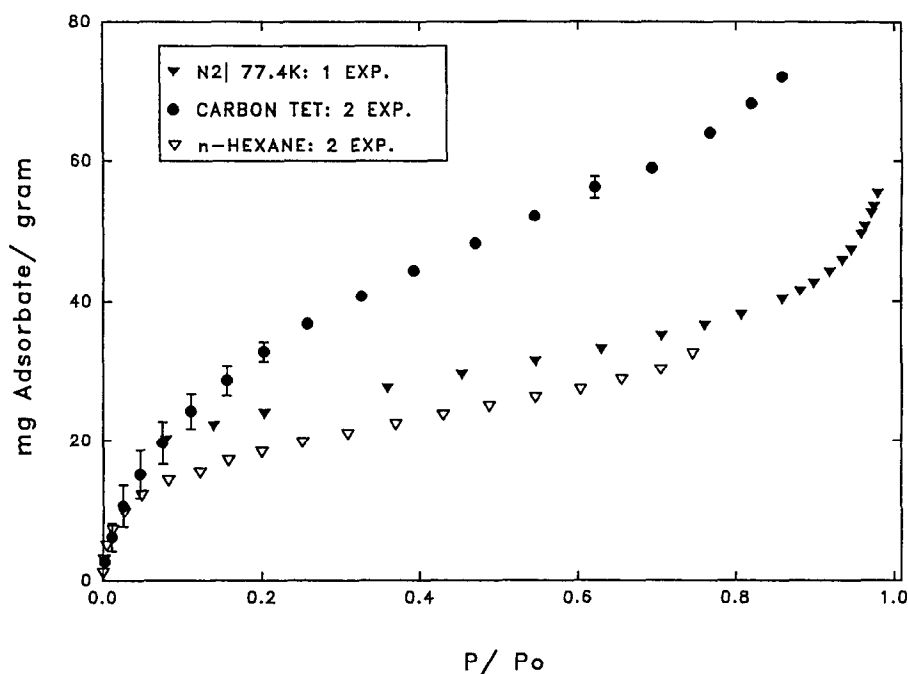


Fig. 2. Adsorption isotherms of  $\text{CCl}_4$ , n-hexane, and  $\text{N}_2$  on Reagan A soil.

In this equation  $M$  is the molecular weight of the adsorbate,  $N_0$  is Avagadro's number, and  $\rho$  is the density of the adsorbate in the liquid phase at the adsorption conditions. For diatomic nitrogen at its normal boiling point, the projected area of a molecule is the generally accepted empirical value of  $0.162 \text{ nm}^2$ . The projected areas of the VOCs at  $27^\circ\text{C}$  were obtained via the equation above. The values of  $X_m$  and  $\alpha_m$  were used to compute the surface area  $S_m$  covered by a unimolecular layer

$$S_m = \left( \frac{X_m N_0}{M} \right) \alpha_m \quad (4)$$

Experimental adsorption data were reduced and plotted as  $X$ , mass adsorbed in mg of adsorbate per g of adsorbent, versus normalized gas-phase concentration  $P/P_0$ . Typical isotherms at  $27^\circ\text{C}$  for the soils are given in Fig. 1 and Fig. 2, Fig. 3, and Fig. 4, and adsorption isotherms for clay minerals are available in Campagnolo and Akgerman [12]. Adsorption isotherms from other soils examined (Table 1) were essentially similar to those in Fig. 1 and Fig. 2. All isotherms had the characteristic Type II shape. Error bands shown in these figures are one standard deviation around the mean. The parameters are calculated from the adsorption isotherm using the BET model, and the correlation coefficients of linear regression and the surface areas computed by Eq. (4) for the two soils in Fig. 1 and Fig. 2 are given in Tables 4 and 5. The BET parameters for the clay minerals and other soil constituents examined are given in Campagnolo and Akgerman [12]. The values for each adsorbate-adsorbent system are the average of the experiments performed.

Table 4  
BET parameters computed from adsorption isotherms of VOCs and nitrogen on Highbanks A soil

Adsorbate	Parameters from the BET model					VOC or N <sub>2</sub> BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Surface area normalized to N <sub>2</sub> area (S <sub>m</sub> /S <sub>N2</sub> )
	X <sub>m</sub> (mg g <sup>-1</sup> )	C <sub>BET</sub>	(P/P <sub>0</sub> ) <sub>m</sub>	r <sup>2</sup>	-ΔH <sub>m</sub> (kJ mol <sup>-1</sup> )		
N <sub>2</sub> at 77.4 K	19.9	163.8	0.07	1.000	8.9	69.3	1.00
n-pentane	15.4	19.5	0.18	0.999	33.6	47.4	0.68
n-hexane	18.0	30.2	0.16	0.999	40.0	50.5	0.73
n-heptane	18.6	32.0	0.15	0.999	44.7	48.7	0.70
benzene	22.7	27.6	0.16	0.999	41.8	53.7	0.77
toluene	21.9	23.0	0.17	0.996	45.8	49.6	0.72
methanol	26.7	53.0	0.12	0.998	47.9	90.6	1.31
CCl <sub>4</sub>	36.7	15.5	0.20	0.998	38.0	46.4	0.67
chloroform	33.1	19.5	0.18	0.999	38.9	48.0	0.69
CH <sub>2</sub> Cl <sub>2</sub>	27.9	17.0	0.20	0.998	35.4	48.8	0.70

One deficiency of the original two-parameter BET equation given above is that it implicitly allows infinite adsorption as the gas-phase pressure goes to the saturation limit. Thus it cannot be used as a model for describing the entire adsorption isotherm. This shortcoming was addressed shortly after the publication of the original BET theory. The modification of the BET theory, recognizing adsorption in a confined space, was published subsequently by Brunauer et al. [17], and is sometimes referred to as the BDDT equation or the three-parameter BET equation

$$\frac{X}{X_m} = \left( \frac{C_{\text{BET}} y}{1 - y} \right) \left[ \frac{1 - (n + 1)y^n + ny^{n+1}}{1 + (C_{\text{BET}} - 1)y - C_{\text{BET}}y^{n+1}} \right] \quad (5)$$

where  $n$  is the number of adsorbed layers. This equation can be used to characterize the entire adsorption isotherm, and in practice it yields values of  $X_m$  and  $C_{\text{BET}}$  similar to those from the above two-parameter model. Hence, BET surface areas derived from the two- and the three-parameter model usually have approximately the same value.

### 3.2. Data analysis

Fig. 3 and Fig. 4 demonstrate the reduction of the isotherms for all adsorbates on the adsorbent (here Highbanks A and Reagan A soils) to approximately a common curve by

Table 5  
BET parameters computed from adsorption isotherms of VOCs and nitrogen on Reagan A soil

Adsorbate	Parameters from the BET model					VOC or N <sub>2</sub> BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Surface area normalized to N <sub>2</sub> area (S <sub>m</sub> /S <sub>N2</sub> )
	X <sub>m</sub> (mg g <sup>-1</sup> )	C <sub>BET</sub>	(P/P <sub>0</sub> ) <sub>m</sub>	r <sup>2</sup>	-ΔH <sub>m</sub> (kJ mol <sup>-1</sup> )		
N <sub>2</sub> at 77.4 K	19.3	296.5	0.06	0.999	9.2	67.0	1.00
n-hexane	15.6	54.8	0.12	0.999	41.4	44.0	0.66
CCl <sub>4</sub>	32.4	16.0	0.20	0.999	38.2	41.0	0.61

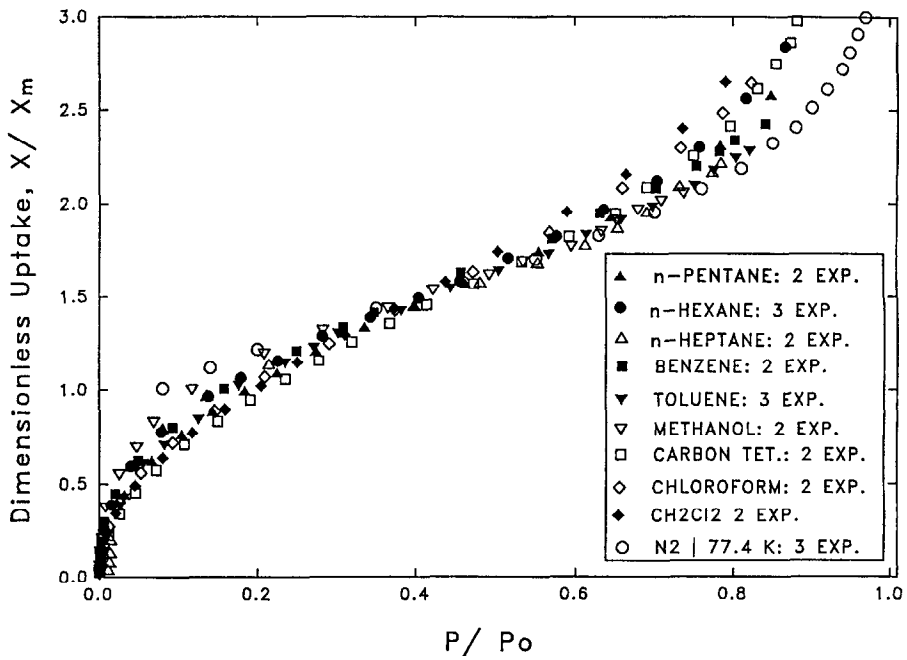


Fig. 3. Reduced adsorption isotherms for Highbanks A soil.

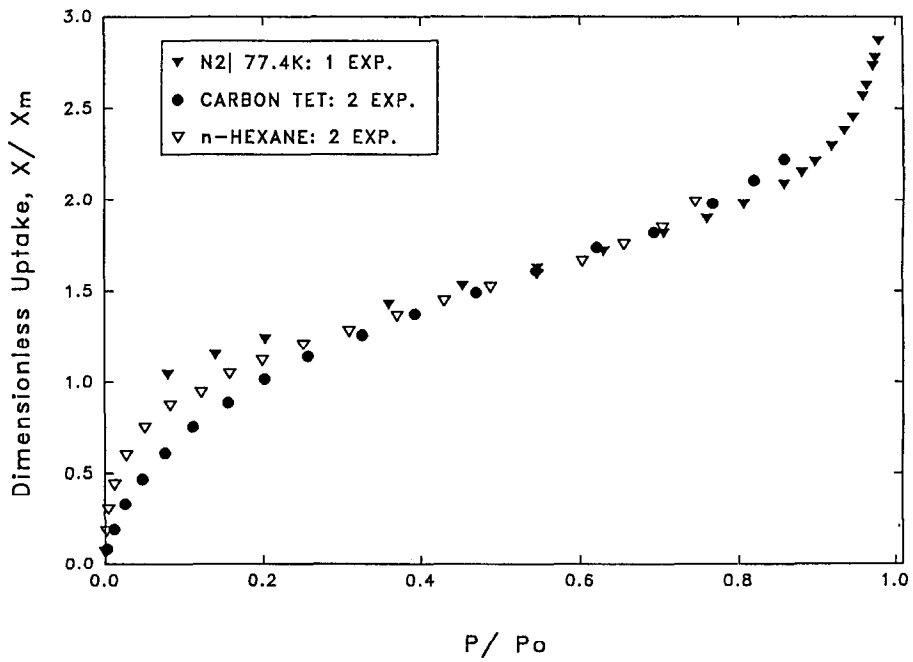


Fig. 4. Reduced adsorption isotherms for Reagan A soil.



expression of the ordinate as a dimensionless quantity: mass adsorbed divided by the amount adsorbed corresponding to the estimated BET monolayer,  $X/X_m$ , which is sometimes referred to in the literature as the statistical number of adsorbed layers. Other adsorption isotherms for VOCs on various soil and soil constituent adsorbents are essentially similar to the above figures in demonstrating the reducibility of isotherms to a common curve by division by the theoretical BET monolayer  $X_m$ .

In Fig. 5, the adsorption isotherms of hexane on various adsorbents (soils and clay minerals) are compared. Again the ordinate is expressed in the statistical number of adsorbed layers  $X/X_m$ . In absolute terms the soils and clays are quite different adsorbents with standard surface areas ranging from  $20 \text{ m}^2 \text{ g}^{-1}$  to a maximum of  $285 \text{ m}^2 \text{ g}^{-1}$ , but the reduced ordinate demonstrates their similarity. The variation in the sharpness of the “knees” of the reduced isotherms appears to be related to the strength of attraction of the surface for the adsorbate. This appears to be related to the charge per formula unit of the clay minerals (Table 2). For instance, kaolinite, having zero charge, has a comparatively gradual slope ( $C_{\text{BET}} = 6.4$ ) in the initial portion of the isotherm, whereas the clay mineral illite, with a typical charge of 0.6–0.9 mol (electrons) per formula unit, has the most pronounced knee ( $C_{\text{BET}} = 71.4$ ). The intermediate charge clays and soils have isotherms which fall between the two extremes. A similar range for  $C_{\text{BET}}$  was also observed by Valsaraj and Thibodeaux [4].

It is noteworthy that all the reduced isotherms for a given adsorbent in Figs. 3–5 unite at approximately  $P/P_0 = 0.4$ , which is taken as the upper limit at which the monolayer is completed and also the vicinity where the desorption and adsorption

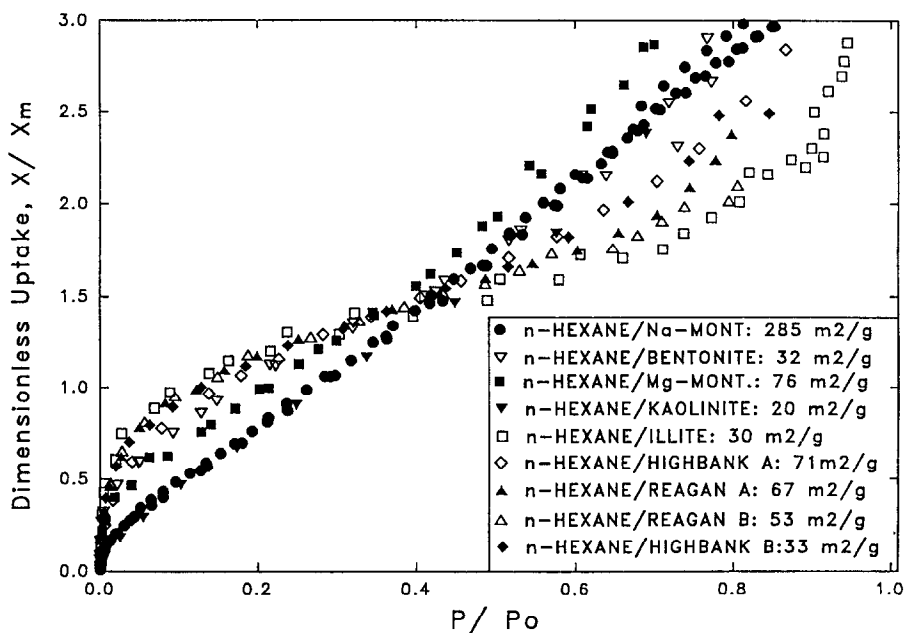


Fig. 5. Reduced isotherms for n-hexane on soils and clay minerals.

isotherms usually recombine. Generally, below this point the values of  $X/X_m$  increase with increasing  $C_{\text{BET}}$  values, but above  $P/P_0 = 0.4$  the situation is reversed and the curves with the lower  $C_{\text{BET}}$  values have the higher number of statistical adsorbed layers, represented by  $X/X_m$ .

### 3.3. Proposed method for prediction of isotherms

The analysis presented for a priori prediction of the isotherms is here limited to non-polar VOCs, i.e. organic chemicals with high volatility and low ratios of dipole moment to molecular weight. This classification thus covers not only those molecules with zero dipole moment (e.g., *n*-hexane or carbon tetrachloride), but also molecules with low dipole moments (e.g., toluene) and those with relatively large moments but also comparatively high molecular weight (e.g., chloroform). VOCs that have hydrogen-bonding capacity, on the other hand, have different adsorption characteristics. An example of a polar VOC would be methanol, which can hydrogen-bond. This distinction is made because the adsorption of non-polar molecules involves primarily, if not entirely, non-specific forces of physical adsorption: dispersion, repulsion, and polarizability [18]. On the other hand, the adsorption of molecules classified as polar adsorbates onto ionic surfaces, such as soil minerals, involves (in addition to the non-specific forces) specific electric forces: dipole, quadrupole, and adsorbate–adsorbate interactions. However, a very large number of the common contaminants from fuels and solvents belong in the non-polar classification.

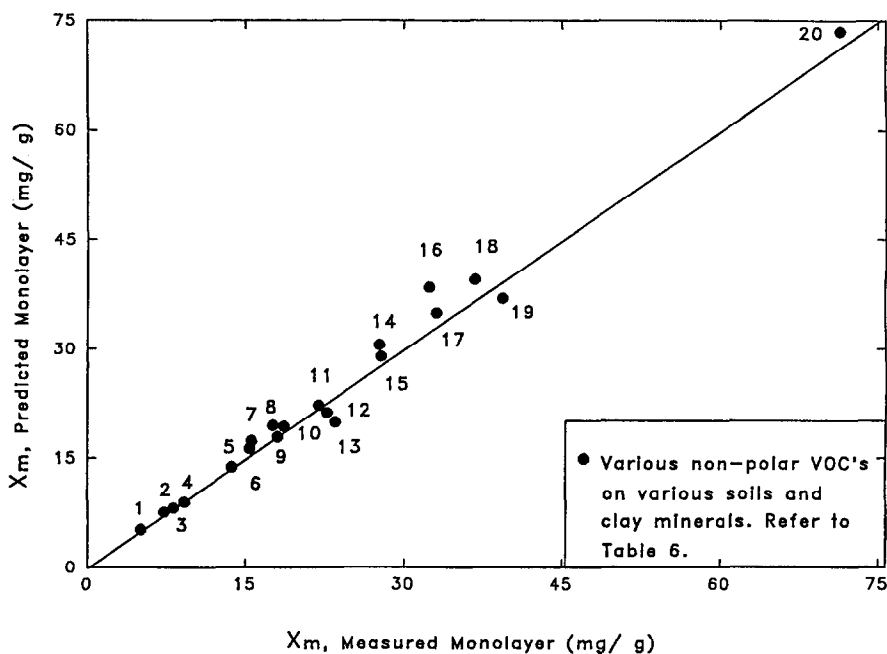


Fig. 6. Parity plot of predicted and measured monolayer amounts  $X_m$ . (Numeric designators refer to Table 6).

The simplest prediction technique is the result of the observation presented in Fig. 3 and Fig. 4; namely, for a given adsorbent, the adsorption isotherms of different species collapse into a single isotherm when plotted as reduced quantities, i.e.  $X/X_m$  vs.  $P/P_0$ . For non-polar VOC adsorption onto a soil or a soil clay mineral at ambient temperature, it was consistently found that the BET surface area was  $\approx 0.70$  times the standard  $N_2$ /BET value (at the boiling point of that adsorbate) [12].

$$X_{m,\text{VOC}} \approx \left( \frac{0.70 M S_{m,N_2}}{\alpha_{m,\text{VOC}} N_0} \right) \quad (6)$$

A parity plot of the predicted compared to the experimental monolayer adsorbed amounts,  $X_m$ , derived from the data is given in Fig. 6 in conjunction with Table 6. This includes all the adsorption systems for all clay minerals and soils mentioned in this document, and for all VOCs listed in Table 3 except methanol. The tabulated data can be seen to support this observation except in the case of methanol (Table 4), where the computed surface area actually exceeds the standard nitrogen estimate. As discussed above, this is expected, as the forces contributing to adsorption in this case include additional phenomena such as adsorbate–adsorbent interactions. However, with the other adsorbates, the standard surface area in conjunction with the hexagonal closest-packing estimate, Eq. (3) in accordance with Eq. (4), can be used to compute the VOC unimolecular layer adsorbed amount at ambient temperature (300 K). Thus, provided that a standard  $N_2$ /BET adsorption isotherm is available in terms of amount adsorbed

Table 6  
Numeric designators for Fig. 6

Point number	Adsorbent	Adsorbate
1	Kaolin	n-hexane
2	Illite	n-hexane
3	Bentonite	n-hexane
4	Highbanks B	n-hexane
5	Reagan B	n-hexane
6	Highbanks A	n-pentane
7	Reagan A	n-hexane
8	Montmorillonite	n-hexane
9	Highbanks A	n-hexane
10	Highbanks A	n-heptane
11	Highbanks A	toluene
12	Highbanks A	benzene
13	Highbanks B	$CCl_4$
14	Reagan B	$CCl_4$
15	Highbanks A	$CH_2Cl_2$
16	Reagan A	$CCl_4$
17	Highbanks A	$CHCl_3$
18	Highbanks A	$CCl_4$
19	Montmorillonite	$CCl_4$
20	Montmorillonite	n-hexane

vs. the relative partial pressure  $P/P_0$ , which is a standard technique, then the adsorption isotherm of the VOC can be constructed from

$$X_{\text{VOC}} = X_{\text{N}_2} \left[ \frac{X_{\text{m},\text{N}_2}}{X_{\text{m},\text{VOC}}} \right] \quad (7)$$

at the same  $P/P_0$  where  $X_{\text{m},\text{VOC}}$  is obtained from Eq. (6). Fig. 7 shows the prediction of the  $\text{CCl}_4$  adsorption isotherm on Reagan A soil (dashed line marked calc-meth1) from nitrogen adsorption data presented in Fig. 2. Although the prediction is good at high concentrations, it deviates significantly from the data at the “knee”. This is because of the very different  $C_{\text{BET}}$  values for nitrogen and  $\text{CCl}_4$  (Table 5).

A more accurate prediction technique necessitates a priori prediction of all three BET parameters. If, as indicated by all the data in this study, the value of  $X/X_m$  at  $P/P_0 = 0.4$  (from here on denoted by  $Q_{0.4}$ ) is the same value for a natural adsorbent over a broad range of VOC adsorbates, then the relationship between the  $C_{\text{BET}}$  and the theoretical number of layers  $n$  is established by use of the three-parameter BET or BDDT model as

$$(0.4)^n \left( n + \frac{5}{3} - Q_{0.4} \right) = \frac{5}{3} \left( 1 - \frac{3}{5} Q_{0.4} - \frac{9}{10} \frac{Q_{0.4}}{C_{\text{BET}}} \right) \quad (8)$$

As implied by this equation, an estimate of the statistical number of layers existing at a normalized gas-phase saturation of 0.4 and also of the  $C_{\text{BET}}$  parameter yields an estimate of  $n$ . This, then, suggests that estimates of the three BET parameters required to characterize completely the isotherm of an adsorbate for which data are not available may be obtained from data for other adsorbates on the same adsorbent. Hanna et al. [19] have noted a similar junction in this vicinity from their experiments for oxygen adsorption onto mineral oxides, but other reports in the literature indicate that this is not

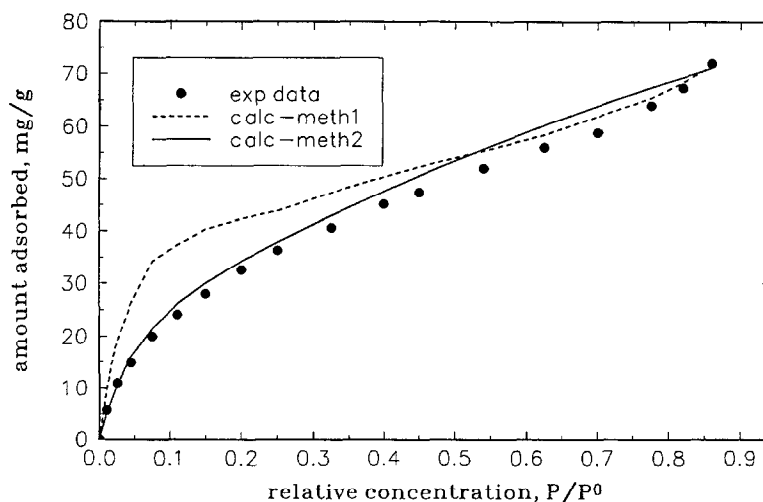


Fig. 7. Prediction of  $\text{CCl}_4$  adsorption isotherm on Reagan A soil.

necessarily a fixed position [20]. If the data were to indicate that a junction point occurs at a different normalized pressure, then a new equation would have to be derived in the same manner as Eq. (6).

As noted above, the value of  $Q_{0.4}$  is a common point among the reduced isotherms of non-polar VOCs on the same adsorbent. Thus it can be obtained from non-polar VOC data. An estimate of the  $C_{\text{BET}}$  value of an adsorbent–adsorbate pair for which no experimental data are available can in some cases be made using isotherm data from other members of the homologous series to which the adsorbate of interest belongs, provided that the data are for the same adsorbent. For adsorption onto a common adsorbent, Barrer [21], working with zeolites, and Kiselev [22], for carbon black, demonstrated that the isosteric heat of adsorption of alkanes and alkenes vary generally as smooth curves with the number of carbon atoms in the adsorbate. Similarly, for adsorption on the soils of this study, as exemplified by the data for Highbanks A (Table 4), the variation in net heat of adsorption  $\Delta H_m$ , as determined from BET analysis for near members of the homologous alkane series, follows a smooth curve. Each increment in net heat of adsorption in the table is due primarily to the change in heat of condensation (vaporization) or, in other words, the  $C_{\text{BET}}$  values for the alkanes examined are not very different. This is not to say that the  $C_{\text{BET}}$  value yields accurate estimates of heat of adsorption, but only that near members within a class of organic chemicals yield  $C_{\text{BET}}$  values within a narrow range. The chlorinated methanes on Highbanks A (Table 4) also illustrate the similarity in  $C_{\text{BET}}$  values for chemicals of a series. Generally, as a first approximation, it can be assumed that near members of a non-polar homologous series will have the same  $C_{\text{BET}}$  value. Interpolation may slightly improve the accuracy of the estimate. Once in possession of an estimate for  $C_{\text{BET}}$ , Eq. (6) can be used to obtain an estimate for  $n$ . Plotted in Fig. 7 is also the isotherm constructed by using a  $C_{\text{BET}}$  of 17.3, which corresponds to  $n = 3.57$  through Eq. (8) and

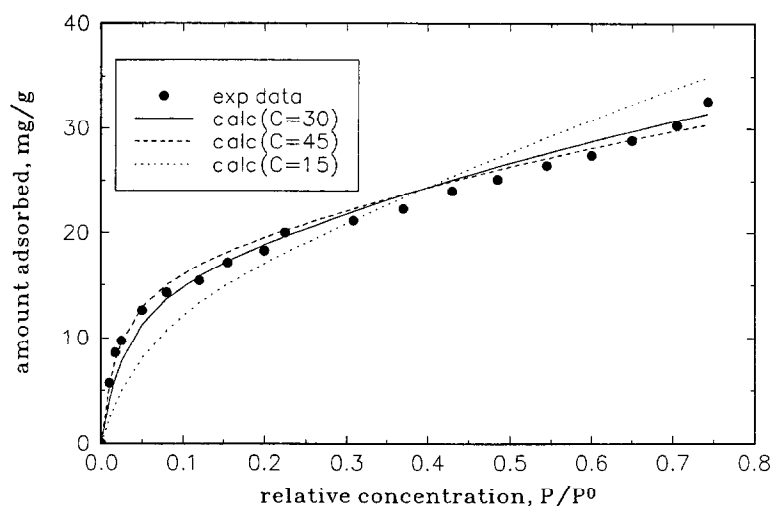


Fig. 8. Prediction of hexane adsorption isotherm on Reagan A soil and the effect of  $C_{\text{BET}}$  parameter.

$X_m$  calculated from Eq. (6) (solid line marked calc-meth2). The  $C_{\text{BET}}$  value was obtained by averaging the  $C_{\text{BET}}$  values for chloroform, carbon tetrachloride and methylene chloride for adsorption on Highbanks A soil (Table 4).

Figs. 3–5 give evidence that, above a  $C_{\text{BET}}$  value of  $\approx 15$ , a large error in the estimate does not have great impact on the shape of the isotherm's "knee", as it is the  $\ln C_{\text{BET}}$  which is related to the attractive energies. Fig. 8 shows data on hexane adsorption on Reagan A soil together with predictions using different  $C_{\text{BET}}$  values of 15, 30, and 45 with corresponding  $n$  values of 3.8, 3.1, and 2.9. Again,  $X_m$  is calculated from Eq. (6). The value of 30 is from data on Highbanks A soil given in Table 4 and the values of 15 and 45 are  $\pm 50\%$  error estimates. All  $C_{\text{BET}}$  values give quite accurate prediction of the experimental data.

#### 4. Summary

The method presented here for a priori prediction of adsorption isotherms is empirical in nature and is based on experimentally observed behavior. However, even if statistical-mechanical methods of theoretically predicting isotherms for well characterized adsorbents do improve in the next decade, there is no guarantee that this will lead to improvement in VOC–soil isotherm prediction because the nature of soils, specifically soil clay minerals, cannot be very exactly described a priori. Thus methods like this empirical one within a theoretical adsorption model framework are perhaps the best to be achieved.

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