

EQUILIBRIUM ADSORPTION OF CHEMICAL VAPORS ON SURFACE SOILS, LANDFILLS AND LANDFARMS — A REVIEW

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Summary

The equilibrium adsorption of Volatile Organic Chemicals (VOCs) onto soils, such as occurring in surface soils, landfills and landfarms, is reviewed. On the basis of moisture content, soils can be classified into the "dry", "damp" and "wet" categories. Increasing moisture content in dry soils is known to lead to displacement of adsorbed nonpolar VOCs. This review addresses adsorption models for the three soil moisture regimes. An extended Brauner, Emmet, Teller (BET) adsorption theory is used and simplified isotherms are developed from it that enable the estimation of partial pressures of VOCs above soils. Available experimental data on VOC adsorption in the present context are also reviewed.

Introduction

Volatile Organic Chemicals (VOCs) stored in landfills have the potential of volatilizing through the soil cover and eventually entering the air. VOCs in landfarms and surface soils have a less restrictive pathway to the air. In either case, during the transport of the VOCs through the soil, they can undergo a variety of transformations such as biodegradation, adsorption onto the soil, dissolution in the soil water and leaching into the groundwater. Of these processes, the one that is of particular interest in the present work is adsorption onto the soil. Adsorption onto soil is one of the important processes which controls the mobility of VOCs through the soil. Adsorption can be both physical and chemical in nature; however under natural environmental conditions and ambient temperatures, the predominant process is physical adsorption of VOCs. This involves forces which are of the London or Van der Waals type. They are mainly of the dispersive type, (induced dipole–induced dipole) polarized forces and short range repulsive forces. Chemisorption of VOCs is rarely seen since they involve actual chemical bonding between the adsorbate and the adsorbent and is an energy intensive process often occurring only at high temperatures [1].

Soil matter consists mainly of mineral fractions, natural organic matter and pore water. Mineral matter which is predominantly montmorillonite, illite or kaolinite and the organic matter provide large surface areas upon which physical adsorption and/or partitioning of molecules can occur. The amount of water in the soil often affects the adsorption process in several ways. It was convenient in this study to use soil water content to classify and define three regimes of adsorption. The three classes of soil were “dry” soil, “damp” soil and “wet” soil. (i) “Dry” soil where the water content is so small that it plays no part in adsorption, (ii) “damp” soil where the water content is not negligible, nevertheless is less than that required to form a monomolecular layer and (iii) “wet” soil where the water content is appreciably large. Figure 1 illustrates the physical adsorption process on a molecular level.

At very low water contents (less than that required to form a monolayer) water can effectively compete with the volatile organics for adsorption sites on both mineral and organic matter and can therefore decrease the adsorption of

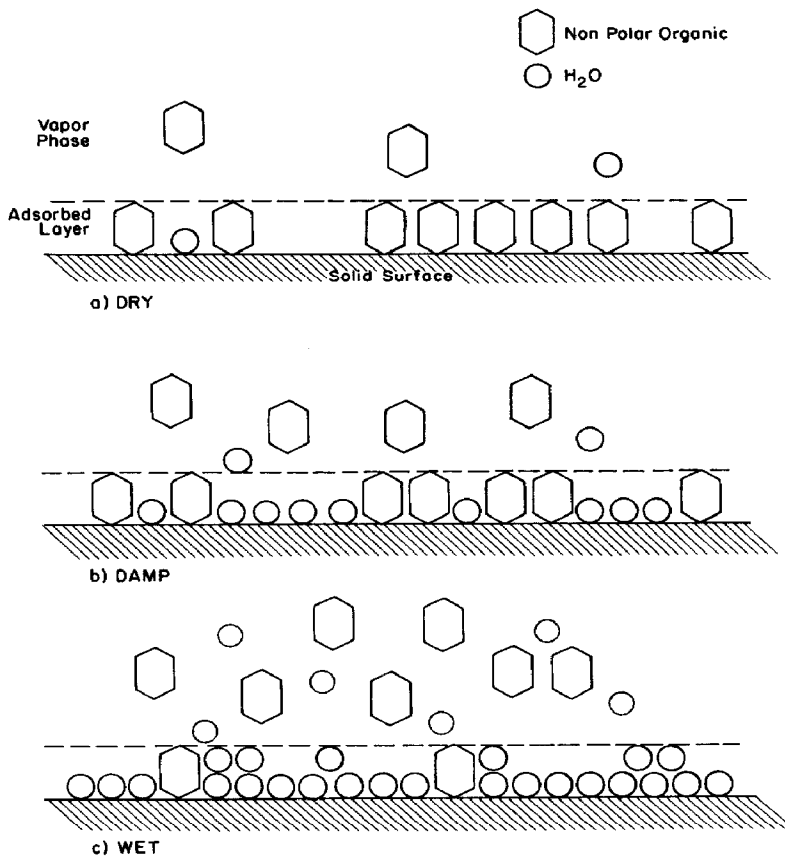


Fig. 1. Illustration of VOC adsorption with three moisture regimes.

VOCs. On “dry” soil, a large amount of VOCs can be adsorbed with little or no competition from water molecules. When the water content increases to a level near that required for a monomolecular layer, the mineral and natural organic fractions are capable of being wet by water and hence restrict the adsorption of VOCs, one reason being that both water and mineral fractions are more polar than most VOCs. However, under such conditions the VOCs, most of which are nonpolar or very slightly polar can partition between water and the natural organic matter in the soil, for which the VOCs have a larger affinity than water. Thus we see that depending on the soil water content, the nature and degree of adsorption of VOCs can also vary. Soil acts as a dual sorbent—mineral matter acting as a conventional adsorbent and the organic matter acting as a partitioning medium. The adsorption of vapors and gases on solid surfaces is usually described well by the Brauner–Emmett–Teller (BET) equation. It also provides the necessary theoretical framework to estimate the equilibrium vapor pressure of VOCs sorbed onto dry soil. A good review is the original work [2] and a more lucid explanation is given by Adamson [1]. The BET model is essentially an extension of the Langmuir model for monolayer adsorption to multimolecular layer adsorption. Although soil is a mixture of mineral and natural organic matter, the BET model assumes all constituents to be made up of similar “solid” surfaces and that physical adsorption of vapors leads to close-packed two-dimensional layers. Although highly idealized, the model does provide a means of estimating the vapor pressure on dry soils.

The original BET isotherm was derived for a single component. However, in certain cases where multicomponent adsorption is concerned (as in the moist soil case) the BET isotherm has to be modified. Although the modified BET isotherm is complex, one can make simplifying assumptions to arrive at simple and useful approximations. Also, the general multicomponent BET isotherm should readily reduce to the original BET isotherm for a single component. Such a derivation is available in the literature and was proposed by Hill [3,4]. We shall take this as our starting point and show how the generalized BET isotherm with simplifying assumptions can lead to simple and more common isotherms. We shall also review existing literature on the adsorption of VOCs and other hydrophobic organic molecules on dry soils. This work may therefore be considered a first step in providing a general set of adsorption isotherms for modeling the chemodynamics of VOCs in soils.

Generalized BET isotherm

In two classic papers in 1946, Hill derived an equation for multimolecular layer adsorption of a mixture of gases on a solid surface based on the BET theory [3,4]. This equation serves as the starting point in our development. Several assumptions and simplifications were required to transform Hill's fi-

nal equation to one that served our purpose. The following paragraph outlines the derivation.

The original equation reflects a model where gas molecules are assumed to be physically attached to the solid surface and that molecules of the second and higher adsorbed layers have the evaporation–condensation properties of a liquid mixture. The model accommodates a variable number, n , of adsorption layers. For more details, the reader is referred to the original references [3,4]. The following assumptions and simplifications were made.

- the gas mixture is binary with A being the VOC molecules of interest and B being water molecules.
- the number of adsorption layers may be infinite ($n \rightarrow \infty$).
- the layer adjacent to the solid surface is the only one different from all other layers which are generally similar.
- the influence of the solid surface dies out as the number of layers increases and hence multimolecular adsorption on these layers is equivalent to condensation of vapors of A and B.

Using these assumptions Hill's original equation reduces to

$$\frac{W_A}{W_{mA}} = \frac{X_A [Q_A (1 - X_B) + X_B Q_B]}{(1 - X_A - X_B) [1 + X_A (Q_A - 1) + X_B (Q_B - 1)]} \quad (1)$$

where W_A is the amount of A adsorbed per gram of solid (g_A/g), W_{mA} is the amount of A adsorbed per gram of solid to form a single monomolecular layer (g_A/g), X_A is the ratio of partial pressure (P_A) to pure component vapor pressure (P_A°) for the VOC, X_B is the similar pressure ratio for water, Q_A and Q_B represent the terms that account for the energy of adsorption for molecules on the solid surface. Each are expressed in heat of adsorption variables:

$$Q_A = \exp [(q_A - q_{AA})/RT] \quad (2a)$$

$$Q_B = \exp [(q_B - q_{BB})/RT] \quad (2b)$$

where q_A and q_B are the heats of adsorption per mole of A and B respectively on the solid surface, q_{AA} and q_{BB} are the heats of condensation of A on A and B on B respectively. R is the gas constant and T is the absolute temperature.

Hill [3] emphasized that there is a limit to the applicability of his equation, the restriction was $(X_A + X_B) \ll 1$. This means that the equilibrium vapor pressures of A and B in contact with the solid are quite small such that $(P_A/P_A^\circ + P_B/P_B^\circ) \ll 1$.

When $X_B = 0$, eqn. (1) reduces to the conventional BET isotherm for a single component adsorbing onto a solid surface

$$W_A/W_{mA} = X_A Q_A / \{ (1 - X_A) [1 + X_A (Q_A - 1)] \} \quad (3)$$

Further discussion and development will be focused on eqns. (1) and (3). It should be noted that neither of these two equations need be used in its entirety.

Simplifications are sought and hence the final equations all have sound theoretical origin.

Review of adsorption and proposed isotherms for various soil types

The purpose of this article is not an extensive review of the entire literature on adsorption of vapors and gases on soil surfaces but only to illustrate the nature of the data and to recommend isotherms to represent the adsorption on soils of various moisture contents. Our discussion was primarily influenced by the necessity to derive simple but quantitative models which can be used to obtain order of magnitude or better estimates of vapor concentrations of chemicals above soils.

Dry soil

We define "dry" soils here as those in which the moisture content is negligibly small such that it plays little or no role in adsorption of organic vapors. In such cases, the single component BET isotherm, (eqn. (3)) has been shown to describe the adsorption of VOCs [5-7]. Data on the adsorption of VOCs of environmental interest in this soil regime is very limited. It has been reported in the literature that pesticide adsorption by dry soils is quite large as compared to wet soil [8,9]. Wade [10] and Call [11] studied the adsorption of the fumigant ethylene dibromide (EDB) on dry soil. Jurinak and Volman [5] studied EDB adsorption in greater detail and reported that the adsorption can be well represented by a BET isotherm. The adsorption of a pesticide (dieldrin) on air-dry soil was reported by Spencer et al. [12]. However, in the realm of volatile organics of environmental interest, there are only two studies reported [6,7]. It was once again observed that BET equation described the isotherms very well. The results of these works are presented in Table 1 along with the BET constants Q_A and W_{mA} in eqn. (3). Equation (3) is, generally valid only for values of $0.01 < X_A < 0.35$. For higher pressure ranges, a three-constant BET isotherm is recommended [1,2,7].

We will now show how some of these observations along with the BET constant may be used to obtain vapor pressures of organic compounds above dry soils. In order to do so one should first obtain estimates of monolayer capacities W_{mA} and soil surface areas. The latter are usually obtained using methods like adsorption of nitrogen, glycol retention, etc. Some of the values of W_{mA} are summarized in Table 2. For most environmental estimates of adsorption, it is helpful if one can estimate the total soil surface areas without resorting to experimental determinations. We propose here one possible method.

Bailey and White [13] gave a review of adsorption of pesticides by soil colloids. The mineral fraction is composed of crystalline clay minerals and crystalline oxides and hydroxides. Table 3 lists the surface areas of various soil constituents compiled by various authors [13,14]. It shows that organic mat-

TABLE 1

BET constants and single layer coverage areas for selected compounds and dry soils

Soil type	Compound	Q_A	W_{mA} (mg/g)	Ref.
Yolo silty clay ^a	Ethylene dibromide (EDB)	73.4	35.9	5
Yolo loam ^a	Ethylene dibromide	96.2	18.7	5
Salinas clay ^a	Ethylene dibromide	59.9	23.9	5
Meloland clay loam ^a	Ethylene dibromide	41.3	26.3	5
Hanford sandy loam ^b	Ethylene dibromide	15.0	3.69	5
Aiken clay loam ^c	Ethylene dibromide	17.1	26.9	5
Staten peaty muck ^c	Ethylene dibromide	12.6	11.7	5
Parsons silt loam ^a	Ether	29.78	5.23	7
Parsons silt loam ^a	Methylcyclohexane	71.45	4.87	7
Parsons silt loam ^a	Dichloropropane	7.82	8.19	7
Parsons silt loam ^a	Benzene	1.84	7.28	7
Parsons silt loam ^a	Methanol	46.46	10.4	7
Weller silty loam ^a	Ether	35.03	8.47	7
Weller silty loam ^a	Methylcyclohexane (MCH)	11.69	9.52	7
Weller silty loam ^a	Dichloropropane (DCP)	32.68	12.7	7
Weller silty loam ^a	Benzene	19.98	11.3	7
Weller silty loam ^a	Methanol	23.43	18.9	7
Summit silty loam ^a	Ether	27.02	4.65	7
Summit silty loam ^a	Methylcyclohexane	98.32	3.34	7
Summit silty loam ^a	Dichloropropane	8.14	8.14	7
Summit silty loam ^a	Methanol	42.96	8.63	7
Bernow sandy loam	Ether	30.24	1.36	7
Bernow sandy loam	Dichloropropane	18.1	1.19	7
Woodburn silty clay ^c	Benzene	13.61	5.57	6
Woodburn silty clay ^c	Chlorobenzene	22.78	7.53	6
Woodburn silty clay ^c	<i>m</i> -dichlorobenzene	24.41	7.42	6
Woodburn silty clay ^c	<i>p</i> -dichlorobenzene	78.48	5.54	6
Woodburn silty clay ^c	1,2,4-trichlorobenzene	27.52	9.53	6

^aMontmorillonitic.^bIllitic.^cKaolinitic

ter, montmorillonite and vermicullite have the highest surface areas. The surface area S (m^2/g) can be estimated by calculation based upon the mass percentage of different constituents in an additive fashion:

$$S = \sum_{i=1}^4 V_i S_i$$
 where V_i is the mass fraction of i th constituent. The four fractions

are sand, silt, clay and organic matter. This is appropriate for dry soil adsorption since it is known that adsorption occurs predominantly on the solid mineral surfaces as discussed by Chiou and Shoup [6] and Poe et al. [7]. From Table 3 it appears that the organic matter and certain clay constituents dom-

TABLE 2

Surface area of dry soils

Soil	Reference compound adsorbed	BET surface area S (m ² /g)	Glycol retention		Ref.
			Total area S_T (m ² /g)	External area S_E (m ² /g)	
Yolo silty clay ^a	EDB	35.9	200	47	5
Yolo loam ^a	EDB	18.7	97	21	5
Salinas clay ^a	EDB	23.9	145	35	5
Meloland and clay loam ^a	EDB	26.3	103	28	5
Hanford sandy loam ^b	EDB	3.69	22	5.2	5
Aiken clay loam ^c	EDB	26.9	93	46	5
Staten Peaty Muck ^c	EDB	11.7	264	20	5
Parsons silty clay ^a	Ether	13.56	-	-	7
Parsons silty clay ^a	MCH	13.65	-	-	7
Parsons silty clay ^a	Benzene	15.66	-	-	7
Parsons silty clay ^a	DCP	14.91	-	-	7
Summit silty clay ^a	Ether	12.73	-	-	7
Summit silty clay ^a	MCH	9.96	-	-	7
Summit silty clay ^a	DCP	13.22	-	-	7
Weller silty clay ^a	Ether	23.89	-	-	7
Weller silty clay ^a	MCH	22.64	-	-	7
Weller silty clay ^a	Benzene	26.58	-	-	7
Weller silty clay ^a	DCP	19.24	-	-	7
Bernow silty sand ^a	Ether	4.08	-	-	7
Bernow silty sand ^a	MCH	4.94	-	-	7
Bernow silty sand ^a	DCP	2.14	-	-	7

^aMontmorillonitic.^bIllitic^cKaolinitic.

inate the surface area with silt and sand fractions having insignificant contributions.

The value of S (cm²/g) calculated (or determined experimentally) as given above is required to estimate the monolayer capacity W_{mA} in eqn. (3). This may be accomplished using the equation proposed by Brauner and Emmett [15]

$$W_{mA} = \frac{S}{f} (d_A^2 M_A / N)^{1/3} \quad (4)$$

where d_A = density of the adsorbate on surface at the concerned temperature, g/ml

M_A = molecular weight of adsorbate, g/mol

TABLE 3

Surface areas of soil constituents

Soil constituent	Surface (m ² /g) ^a	Area <i>S</i> (cm ² /g) ^b
Organic Matter	500-800	
Vermiculite	600-800	
Montmorillonite	600-800	
Diocahedral Vermiculite	50-800	
Illite	65-100	
Kaolinite	7- 30	
Oxides and Hydroxides	100-800	
Silt		454
Very fine sand		227
Fine sand		90.7
Medium sand		45.4
Coarse sand		22.7
Fine sand		11.3

^aBailey and White [13].^bFuller [14].

N = Avogadro's number

The factor f in eqn. (4) has been the subject of much investigation. It is related to the projected area of a molecule on the surface when the arrangement is a close two-dimensional packing. This value is slightly smaller than that obtained by assuming that the adsorbed molecules are spherical and their projected areas on the surface are circular. In most BET experiments, the value of $f=1.091$ suggested by Emmett and Brauner [15] is used. The value of the density, d_A , is normally taken as that of the condensed gas, liquid or solid at the temperature of adsorption. Equation (4) also applies for water vapor adsorption onto the soil.

The BET isotherm (eqn. (3)) still contains one more constant Q_A . This parameter is related to the molar heat of adsorption of the compound upon the mineral and natural organic matter and varies considerably between different soils for different compounds. This is exemplified in Table 1. However certain general trends are apparent, such as large Q_A values for montmorillonitic soils as compared to kaolinitic or illitic soils. Cupitt [16] discussed the adsorption of toxic organic chemicals in the vapor phase upon aerosol particulates in the atmosphere. He reported that the value of Q_A is generally greater than 1 and range from 3 to 26 at 298 K, with the larger values given for butane and the smaller values for inert gases like nitrogen and argon adsorbed onto activated carbon. In his calculation, he assumed a value of $Q_A = 25$ for acrylonitrile, ethylene dichloride, perchloroethylene, vinylidene dichloride and benzo-[a]-pyr-

ene. Pankow [17] showed that available data on the adsorption of hydrophobics on aerosols in Langmuirian in nature. The data by Jurinak and Volman [5], Chiou and Shoup [6] and Poe et al. [7] as presented in Table 1 are of most significance to us as they deal directly with adsorption of VOCs on dry soil. Jurinak and Volman [5] noted distinctly higher values of Q_A for EDB adsorption on montmorillonite ($Q_A = 67.7$ average) as compared to kaolinite (=15 average). The same trend was apparent for other compounds as well, and is given in Table 1. Apparently the adsorptive forces for VOCs on montmorillonitic soils are stronger than those on the kaolinitic soils. It is generally known that for BET adsorption, Q_A values larger than 10 give isotherms of similar sigmoid shape and that under such circumstances the value of monolayer capacity, W_{mA} is the most important parameter [18] in determining the shape of the adsorption isotherm.

For environmental applications, as in landfills and landfarms, where the X_A ($=P_A/P_A^\circ$) values are generally smaller than 0.01 and Q_A values larger than 10 (for most VOCs on montmorillonitic soils), the BET eqn. (3) maybe further simplified to obtain

$$W_A/W_{mA} = X_A Q_A / [1 + X_A Q_A] \quad (5)$$

which is the Langmuir isotherm for monolayer adsorption. Using eqn. (4) in (5), we can then obtain the equilibrium partial pressure of the chemical above dry soil for low concentration levels in the soil as

$$P_A = \frac{P_A^\circ}{Q_A} \left[\frac{W_A/W_{mA}}{1 - W_A/W_{mA}} \right] \quad (6)$$

where $W_{mA} = 0.917 S \epsilon (d_A^2 M_A / N)^{1/3}$. In utilizing this equation one should remember that the values of area, S estimated from Table 2 using an additive approach for fractions of constituents in the soil is the total surface area whereas the actual value of area available for adsorption of most non-polar VOCs would be the external surface area of the soil (Jurinak and Volman [5]; Poe et al. [7]). Therefore S would have to be multiplied by a fraction ϵ which is the ratio of external surface area to total surface area. This has been done in eqn. 6. For example, as per the data provided by Jurinak and Volman [5] for a variety of soils the fraction ϵ is about 0.184 with a standard deviation of 0.072.

In order to illustrate the use of eqn. (7), we chose the data on dieldrin (Molecular weight = 380.9; density = 1.75 g/ml) adsorption on a dry Gila silt loam [12]. The total surface area for adsorption of this soil (18.4% clay-montmorillonite, 0.6% organic matter) was determined by experiment to be 90 m²/g. The saturation vapor pressure of dieldrin at 40°C was reported to be 3.47×10^{-5} mmHg [12]. We chose Q_A to be approximately 40. Then, above a soil containing 1×10^{-4} g dieldrin/g soil, the partial pressure of dieldrin would be

$$P_A = \frac{3.47 \times 10^{-5}}{40} / \left[\frac{0.917 \times 0.184 \times 90 \times 10^4}{1 \times 10^{-4}} \left(\frac{1.75 \times 1.75 \times 390}{6.023 \times 10^{23}} \right)^{1/3} - 1 \right]$$

$$= 4.5 \times 10^{-9} \text{ mmHg.}$$

Thus the calculated value is 0.45×10^{-8} mmHg whereas the experimental value is 8.8×10^{-8} mmHg. Calculated S is $(0.18 \times 700 + 0.006 \times 650) = 133 \text{ m}^2/\text{g}$, which compares relatively well with the experimental value of $90 \text{ m}^2/\text{g}$. Considering the simplifications in the model and the approximations of various terms, this degree of agreement is remarkable. The actual dieldrin partial pressure for this soil loading was 4 orders of magnitude (i.e., 10^4) lower than the pure component vapor pressure and the model predicts this drastically lower value within approximately one order of magnitude. Actually the correspondence is a factor of 20 or 95% lower than the measured value. It should be remembered that if P_A/P_A° is > 0.01 , eqn. (3) has to be used to calculate the vapor pressure above dry soil, and it is generally valid, in most cases, for values of P_A/P_A° up to 0.35.

Damp soil

At low soil moisture levels, of the order of fractions of a percent (wt.) range, soil surface coverage by the sorbed water molecules is small so that large areas of "dry" surface are available as adsorption sites for the less polar organic molecules. This is the situation for the dry case considered above so that the water content and its properties do not enter the model calculations. However, as the moisture level increases (approaches that required for a monomolecular layer of water) water molecules will efficiently compete for adsorption sites. Because of their propensity for adsorption on polar mineral surfaces, water molecules will displace the less polar organic molecules from the surface and thus reduced adsorption is often possible [13]. Spencer and Cliath [19] reported that lindane was completely desorbed from Gila silt loam as the soil moisture content increased to just above that required for a monomolecular layer. For example, at 30°C , a 2.2% water content soil (equivalent to 0.79 of a monomolecular layer) with $43 \mu\text{g}$ lindane adsorbed/g soil, the lindane partial pressure was only 1.52×10^{-8} atm while at 3.94% soil water content the lindane partial pressure increased to 1.51×10^{-7} atm and at 10% water content it was 1.42×10^{-7} atm which is close to the pure component vapor pressure of lindane (1.69×10^{-7} atm). Thus above one monomolecular layer of water the vapor density of lindane approached that of its pure component vapor density. The same effect was noticed for DDT on Gila silt loam [20] and dieldrin on the same soil [21].

Similar effects for volatilization of lindane and DDT from soils have also been reported by Guenzi and Beard [22]. A more recent study by Chiou and

Shoup [6] showed more conclusively the adsorptive displacement of volatile organics (benzene, chlorobenzene, *p*-dichlorobenzene, *m*-dichlorobenzene and 1,2,4-trichlorobenzene) by water from adsorbed sites on a Woodburn soil (21% clay kaolinite, 1.9% organic matter, 9% sand and 68% silt).

Chisolm and Koblitsky [23] found that methyl bromide was adsorbed to a greater extent on dry soils than on wet soils. Hanson and Nex [24] reported similar observations for ethylene dibromide, which was further investigated by Wade [25]. Wade [25] reported that there was a five-fold decrease in EDB adsorption as the moisture content increased from 0 to 18%, a nonlinear decrease up to 40% and a slight apparent increase in adsorption from 40% to 75% moisture content. The latter effect at 40–75% moisture content was attributed to the formation of solutions of EDB in soil water. Ashton and Sheets [26] observed that air-dry soil adsorbed more EPTC (Ethyl *N,N*-di-*n*-propylthiol carbamate) than field capacity soil. Bailey and White [13] summarized the interrelationships between moisture content, adsorption and vapor loss (volatilization) of certain herbicides. Similar summaries on pesticide volatilization potentials were given by Spencer et al. [8,9]. There exist several reports in the literature which suggested that pesticides volatilized more rapidly from wet soil samples than from dry soil [27–34]. All these investigators concluded that water increased the vapor pressure of the organic chemical in the damp soil moisture range owing to competition for adsorption sites. When the soil water content increased sufficiently to cover the soil surface, the vapor density approaches that of the pure material. Igue et al. [35] reported that the air relative humidity also influenced pesticide adsorption on soil indirectly by increasing the soil water content. As suggested by Spencer et al. [9], the soil water content at which pesticide vapor density sharply decreased depended upon the nature of the soil and the adsorption capacity of the pesticide relative to that of the water vapor. Thus, pesticides with stronger adsorption ability will require larger soil water content for displacement from the adsorption sites.

All of the above observations point to the ability of water to compete extensively with the organic compounds for adsorption sites on damp soil. In order to take this effect into account, we may take as our starting point eqn. (1) which is the BET isotherm for binary adsorption. In order to simplify this equation for our purpose of estimating partial pressure of VOCs above landfills, landfarms or surface soils, we required some information about the magnitude of Q_A ($A \equiv \text{VOC}$) and Q_B ($B \equiv \text{water}$) values on common dry soils. The range of Q_A values on predominantly montmorillonitic soils fall between 2 and 80 (Table 1). Kaolinitic and illitic soils have generally smaller Q_A values for non-polar organics.

Extensive investigations have been carried out by Orchiston on the adsorption of water on montmorillonitic and kaolinitic soils, [36,37]. He observed that the BET single component isotherm satisfactorily predicted the adsorption of water vapor on various soils. Table 4 summarizes some of the data

TABLE 4

BET constants for adsorption of water vapor on soils [6,35]

Adsorbent	W_{mB} (mg/g)	Q_B	$(q_B - q_{BB})$ (cal/mol)
<i>Montmorillonite</i>			
Natural unheated	12.56	21.0	1810
Preheated, 105°	11.67	23.3	-
Mg-saturated, unheated	11.67	28.4	-
H-saturated, unheated	11.86	15.2	-
Na-saturated, unheated	9.31	5.9	-
Natural unheated at 35°C	12.07	19.6	-
<i>Illite</i>			
Natural unheated	2.37	12.1	1480
Ca-saturated unheated	2.67	9.2	-
Na-saturated unheated	2.83	8.5	-
<i>Kaolinite</i>			
Natural unheated	0.17	37.8	2160
<i>Sand</i>			
Green sand, unheated	1.89	5.0	955
<i>Woodburn dry soil</i> (21% Kaolinite)			
	11.7	37.66	-

collected by him as well as Chiou and Shoup [6]. It was concluded that the Q_B values for water on both montmorillonitic and kaolinitic soils were larger than unity (in the range 15–40). Thus, because both Q_A and Q_B are sufficiently large and under environmental conditions of low vapor pressure when $P_A/P_A^\circ < 0.01$ and X_B is very small we can reduce eqn. (1) to

$$\frac{W_A}{W_{mA}} = \frac{X_A Q_A}{1 + Q_A X_A + Q_B X_B} \quad (7)$$

which is a modified form of the Langmuir isotherm for binary adsorption. A similar equation holds for water ($\equiv B$)

$$\frac{W_B}{W_{mB}} = \frac{X_B Q_B}{1 + Q_A X_A + Q_B X_B} \quad (8)$$

If the amount of water required to form a monolayer and the amount of adsorbed water (soil moisture content) are known, then W_B/W_{mB} is known. In most practical cases, it is easier to determine the soil moisture content (i.e., W_B/W_{mB}) than it is to know Q_B and X_B . Hence we chose to eliminate the product $X_B Q_B$ between eqn. (7) and (8) to obtain.

$$\frac{W_A}{W_{mA}} = \frac{X_A Q_A (1 - W_B/W_{mB})}{1 + X_A Q_A} \quad (9)$$

Since this is a Langmuir equation, the assumption is that the maximum amount of water W_{mB} corresponds to a monolayer, and hence eqn. (9) is valid only so long as $W_B/W_{mB} < 1$ and $X_A < 0.01$. Note that eqn. (9) indicates that as the soil moisture content increases the adsorptive capacity of the soil for the solute A decrease markedly. Equation (9) may be rewritten as

$$\frac{P_A}{W_A} = \frac{P_A^\circ}{Q_A W_{mA} (1 - W_B/W_{mB})} + \frac{P_A}{W_{mA} (1 - W_B/W_{mB})} \quad (10)$$

Thus by plotting P_A/W_A versus P_A one can obtain both Q_A and W_{mA} from the intercept and slope if W_B/W_{mB} is known.

The use of eqn. (9) to estimate the vapor pressure of VOCs above "damp" soils, therefore, entails numerical values for Q_A , W_A/W_{mA} , and W_B/W_{mB} . W_{mA} may be estimated using equation (4). W_{mB} may be similarly determined by eqn. (4) as shown by Orchiston [36]. Actual soil moisture content can be transformed to obtain W_B [19,20]. The ratio W_B/W_{mB} must be less than unity. This limitation therefore defines the water content range for the "damp" soil model and the conditions under which eqn. (9) can be used. Figures 2a, 2b and 2c show the dramatic effects of soil moisture contents on P_A as obtained from eqn. (9).

If one can obtain the individual adsorption isotherm data for the pure organic solute and pure water separately then one should be able to use the BET equation for binary mixtures to obtain the partial pressure of a mixture of organic vapor and water. A forerunner to such an approach is the work of White et al. [38,39].

The working form of eqn. (9) is:

$$P_A = \frac{P_A^\circ}{Q_A} \left[\frac{W_A/W_{mA}}{1 - (W_A/W_{mA} + W_B/W_{mB})} \right] \quad (11)$$

where $W_B = 0.917 \epsilon S (d_B^2 M_B/N)^{1/3}$. The numerical value of W_B/W_{mB} must be less than unity. If $W_B/W_{mB} = 0$ then eqn. (11) becomes eqn. (6). This occurs when the soil is dry. For water $\epsilon = 1$.

There are other useful models to predict adsorption of gas mixtures [40]. Single solute adsorption isotherms may be used to determine the activity coefficients in the adsorbed phase in equilibrium with the gas mixture based on the assumption of an Ideal Adsorbed Phase [41]. These models are of limited value due to large nonidealities associated with systems where non-polar organic solutes are involved. Highly nonideal systems can be described using the method proposed by Suwanayuen and Danner [42,43].

Wet soil

When the soil water content approaches closely and exceeds a single monolayer coverage of particles, another equilibrium regime occurs. Specifically the wet soil case is that fraction ratio of water content such that $W_B/W_{mB} > 0.95$.

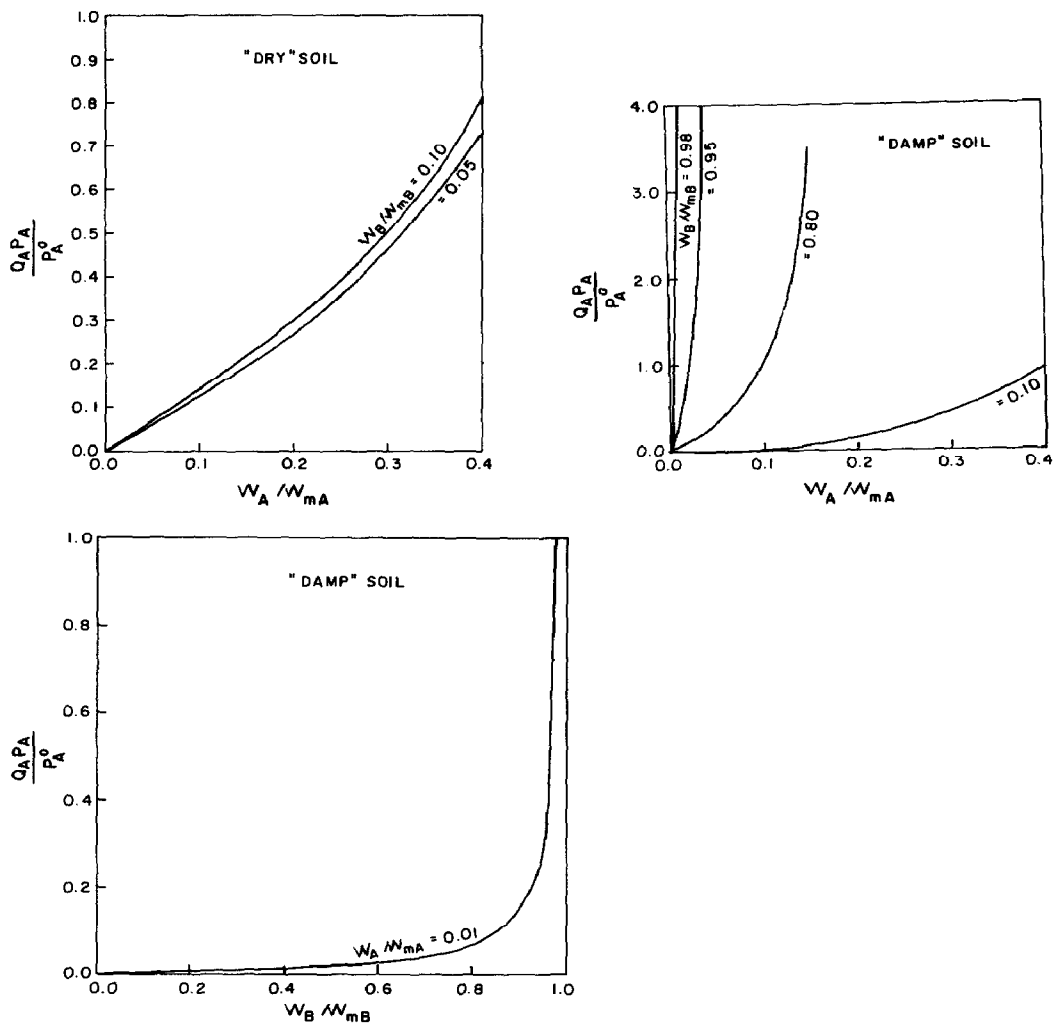


Fig. 2a. Effect of soil moisture content on chemical partial pressure for "dry" soil.

Fig. 2b. Effect of soil moisture content on chemical partial pressure for "damp" soil.

Fig. 2c. Effect of soil moisture content on chemical partial pressure for "damp" (wet) soil.

In this case an aqueous solution is present in the soil pores, the clay and natural organic matter in the soil are completely wet and less available for the adsorption of organic molecules. The natural soil organic matter competes more effectively than clay surfaces for the non-polar hydrophobic molecules [44]. In any event, the adsorptive behavior now becomes more like adsorption or partitioning from aqueous solutions onto natural organic matter.

Adsorption of water on a surface reduces the surface free energy of the soil and therefore decreases the adsorption of other species. Adsorption from an

aqueous phase can be described satisfactorily by a Langmuir equation [1]. Adamson [1] argues further that for heterogeneous surfaces where the energies vary with the nature of the sites the adsorption can be described by an exponential distribution function thus resulting in the Freundlich isotherm equation. This equation frequently appears as:

$$W_A = K_d C_A^{1/n} \quad (12)$$

where C_A is the concentration in the aqueous phase and K_d as well n are constants.

In the case of the equilibrium adsorption of hydrophobic chemicals from water onto soil or sediment the value of $1/n$ has often been close to unity. A recent review [45] gave values on a variety of compounds. If $1/n$ is taken to be unity and applied to solute equilibrium between soil and water eqn. (12) becomes

$$W_A = K_d C_A \quad (13)$$

Numerous investigators have used this simple relationship to describe the equilibrium partitioning of a non-polar hydrophobic compound between the soil organic matter and the aqueous phase. Several authors [46,47] have shown that the soil organic matter content is directly correlated to the sorption of nonpolar organic compounds. The contaminant sorption may also be expressed on an organic carbon (K_{oc}) or organic matter (K_{om}) basis

$$K_{oc} = K_d/f_{oc}; K_{om} = K_d/f_{om} \quad (14)$$

where f_{oc} and f_{om} are organic carbon and organic matter fractions respectively.

There is considerable discussion regarding the point whether the mechanism involved is really an adsorption onto the organic matter or partitioning between the organic matter and the aqueous phase [48]. However, it is fairly well agreed that good order of magnitude estimates of adsorption are possible from such an approach. Frequently the values of K_{oc} or K_d are related to the aqueous solubility (S_{aq}) or the octanol-water partition coefficients for the organics. For example Means et al. [49] suggested the following relationship between K_{oc} and S_{aq} for 4 polychlorinated aromatics on 14 different sorbents

$$\log(K_{oc}) = 0.686 \log(S_{aq}) + 4.723 \quad r^2 = 0.98 \quad (15)$$

while Schwarzenbach et al. [50] gave the following relationship between K_d and K_{ow} for 13 different non-polar organics on 6 different sorbents.

$$\log(K_d) = 0.72 \log(K_{ow}) + \log(f_{oc}) + 0.49 \quad r^2 = 0.95 \quad (16)$$

Rao and Davidson [51] gave the following relationship between K_{oc} and K_{ow} for several pesticides

$$\log(K_{oc}/1000) = 1.029 \log(K_{ow}/1000) - 0.18 \quad r^2 = 0.91 \quad (17)$$

where 1000 is needed because K is expressed in m^2/kg while the regression used ml/g for the units of K . Numerous other correlations are equally applicable.

It should, however be emphasised that such correlations are based on idealized systems and hence should be used with caution if very exact estimates of adsorption are needed.

The above mentioned correlations for partitioning between water and soil organic matter are based on the following important observations:

- (a) linear adsorption isotherms even as the aqueous solubility of the solute is approached,
- (b) the slope of the plot of adsorbed solute concentration versus dissolved solute concentration, i.e., K_d is proportional to soil organic matter fraction,
- (c) relatively small heats of adsorption, and
- (d) little or no adsorptive competition between solutes even as solubility is approached.

The adsorption of a nonpolar organic solute from an aqueous solution is solely due to the hydrophobic nature of the non-polar solute; this being due to the inability of the hydrophobic solute to compete with the strong hydrogen bonds between water molecules [52]. As suggested earlier, adsorption has been mainly attributed to the soil organic matter. However in certain cases such a partitioning concept has been questioned [48]. Also, in case where mineral matter predominates over organic matter, relatively high adsorption has been observed [53]. These observations have been put in perspective by McCarty et al. [53] by suggesting a two phase-partitioning concept such that K_d is given by

$$K_d = f_{if}K_{if} + f_{oc}K_{oc} \quad (18)$$

where f_{if} is the inorganic fraction with K_{if} being the respective partition coefficient. Thus for $f_{if} \ll 1$, $K_d \cong f_{oc}K_{oc}$ whereas for $f_{oc} \ll 1$, $K_d \cong f_{if}K_{if}$.

Kipling [54] noted that the Freundlich equation was also applicable when aqueous concentrations were replaced by pressures or relative vapor pressures. A test of this is a plot of $\log(W_A)$ versus $\log(P_A/P_A^\circ)$ which should be a straight line. This was verified by Spencer and Claith [19] for the adsorption of lindane on water saturated Gila silt loam for soil water contents of 3.94%, 10% and a 5:1 water:soil suspension. The fact that the isotherms for all three water contents were described by the same line suggested that Henry's law was obeyed over the soil-water system when the water contents were more than that required for a monomolecular layer. Thus the ratio of vapor pressure P/P° will also equal the ratio of solution concentration C/C_0 . In other words, a knowledge of soil-water adsorption isotherms for "wet" soil should permit us to estimate the relative vapor pressures in the soil atmosphere. Equation (12) or (13) should therefore prove useful in this regard.

Henry's law describes the equilibrium relationship for chemicals across an

aqueous/air interface in the dilute-solution range. In terms of partial pressure in air and concentration in the aqueous solution the relationship is

$$P_A = HC_A \quad (19)$$

where H is the Henry's constant. Combining eqns. (19) and (13) to eliminate C_A yields

$$P_A = W_A H / K_d \quad (20)$$

This equation shows that there is a simple linear relationship between chemical partial pressure in the gas phase and the chemical concentration on the soil. Such behavior was observed by Spencer and co-workers [8,9,19–21] for the adsorption of various pesticides on Gila silt loam. They also observed that above a certain critical soil loading level or concentration of the chemical no further increase in P_A occurred and that the maximum was P_A° , the pure component vapor pressure.

Obviously in an equilibrium situation the partial pressure of the chemical cannot exceed the pure component vapor pressure so that eqn. (20) has a limit of applicability. If $P_A = P_A^\circ$ then W_A° is the critical value of soil loading. From eqn. (20) then

$$W_A^\circ = P_A^\circ K_d / H \quad (21)$$

and

$$P_A = P_A^\circ \quad (\text{constant}) \quad (22)$$

for $W_A \geq W_A^\circ$, so that pressure is independent of soil concentration. This behavior has been observed for dieldrin, *o,p'*-DDT, trifluralin, lindane and *p,p'*-DDT [55] and occurs at very low values of soil concentration. The respective concentrations on Gila silt loam were 25, 39, 73, 55 and 15 mg/g.

The recommended equations for the "dry", "damp" and "wet" cases are summarized in Table 5. We have attempted a test of these equations to describe the experimental data of various investigators and found them to be satisfactory [56] in estimating the partial pressures of VOCs.

Summary of uses and limitations of the models

We have demonstrated in this review that the adsorption equilibrium process of hydrophobic organics onto soils is tractable and closely related to the moisture content of the soil. A simultaneous review of experimental findings of numerous investigations and the development of model equations based on classical adsorption theory was undertaken. Three cases of soil moisture "dry", "damp", and "wet" evolved as being logical consequences of simplifications of the binary form of the multicomponent extended BET isotherm originally derived by Hill [3,4]. We have shown how simplified equations are developed to

TABLE 5

Adsorption isotherms for various soil conditions

$$\text{Surface area: } S = \sum_{i=1}^4 V_i S_i$$

$$\text{Moisture for monolayer coverage: } W_{mB} = 0.917\epsilon S (d_B^2 M_B / N)^{1/3} \quad (4)$$

$$\text{Chemical for monolayer coverage: } W_{mA} = 0.917\epsilon S (d_A^2 M_A / N)^{1/3} \quad (4)$$

$$0 < \epsilon < 1, \epsilon = 1 \text{ for water}$$

Dry soil case. Definition: $W_B / W_{mB} < 0.05$

Partial Pressure:

$$P_A = \frac{P_A^\circ}{Q_A} \left[\frac{W_A / W_{mA}}{1 - W_A / W_{mA}} \right] \quad \text{for } W_{mA} > W_A \quad (6)$$

Damp soil case. Definition: $0.05 < W_B / W_{mB} < 0.95$

Partial Pressure:

$$P_A = \frac{P_A^\circ}{Q_A} \left[\frac{W_A / W_{mA}}{1 - (W_A / W_{mA} + W_B / W_{mB})} \right] \quad (11)$$

Wet soil case. Definition: $W_B / W_{mB} > 0.95$ (21)

Critical chemical level: $W_A^\circ = P_A^\circ K_d / H$

Partial Pressure:

$$P_A = W_A H / K_d \quad \text{for } W_A < W_A^\circ \quad (20)$$

$$P_A = P_A^\circ \quad \text{for } W_A \geq W_A^\circ \quad (22)$$

describe each of the three situations based on the extended BET theory and these are summarized in Table 5.

The equations in the table are displayed in a format that relates the equilibrium partial pressure of hydrophobic organics as a function of the chemical concentration on soil and the soil moisture content. These are the primary independent variables and this arrangement is useful for engineers, environmental chemists, soil scientists and others interested in numerical estimates of the volatility and volatilization potential of hydrocarbons, chlorinated hydrocarbons, certain pesticides etc., as they exist in the soil environment. Besides the concentration of the chemical and water in the soil, seventeen other quantities are needed. Eight involve the soil alone. These are the external surface area and mass fractions of the sand, silt, clay and natural organic matter components of the soil. Two are related to water and these are its liquid (vicinal) density and molecular weight. Three are related to the chemical, and these include its pure component vapor pressure at soil temperature, liquid (vicinal) or solid density and molecular weight. Three equilibrium isotherm

parameters are needed and these are BET parameter Q_A , the chemical partition coefficient between soil and water, and Henry's constant. The final quantity is ϵ and this is an adjustable parameter that relates the fraction of the external surface area that is available for chemical and water monolayer coverage. It should be noted that Q_A , chemical vapor pressure, partition coefficient and Henry's constant are strong functions of temperature. Extra parameters will be needed to quantify the temperature effects.

Many assumptions were made in arriving at the final equations and aspects of these and the limitations need to be addressed.

The original and extended versions of the BET models assume the adsorbed molecules exist in monomolecular layers one positioned above another. This is an unrealistic model in the case of water adsorption onto soils in that it does not account for surface tension effects within soil capillaries. These effects will cause water to accumulate in the cusp zones around the points of contact of soil particles and other concave niches. This accumulated water increase the total measured moisture content but does not necessarily contribute to increased surface coverage. The use of the measured moisture content will likely result in an overestimation of W_B which in turn elevates the calculated partial pressure of the organic in eqn. (11). A means of accounting for this moisture effect needs to be developed.

All three model equations are valid for low levels of organics sorbed onto the soil solids. These levels are less than one monolayer coverage, i.e., $W_A < W_{mA}$, and is an obvious limitation in eqns. (6) and (11) for the "dry", and "damp" soil cases. The model equations for the "wet" soil case apply well below the solubility limit of the hydrophobic compound. This limit must be recognized for obtaining constant values of the partition coefficient and Henry's constant. The one monolayer limit and the solubility limit are identical concepts in the case of the "wet" soil. Obviously a layer of organic covered by a layer of water produces a solubility limit condition.

The competition of water and organic molecules sorbed onto the soil surface is handled in a highly idealized fashion to yield the "damp" soil model. The BET script calls for the treatment of each species separately without interaction. It is unlikely that water and organic species can exist side-by-side in area-patches of molecules without any solution of the organic in the water and vice-versa. However, the BET parameter Q_A in eqn. (11) is assumed to be the same as that in eqn. (6) for the single species case. The limitations of this assumption needs to be explored by carefully conceived and executed experiments and the effects on Q_A quantified.

The linear addition of the surface area fractions to yield the total for molecular adsorption is a mathematical convenience that contains some implications that need clarification by experiment as well. This is a highly idealized approach. Surface areas measured by N_2 adsorption and ethylene glycol adsorption are known to yield different quantities and neither are usually equal

to the surface area occupied by the organic of interest. The creation of ϵ to account for these inequalities is a convenient fudge factor at this point. It is also unlikely that ϵ will be of the same numerical value for water, which is polar and the hydrophobic organic on the same soil surface. It is obvious that the ϵ factor and other fuzzy aspects of the models will need to be fully explored and quantified in order to yield a more defensible adsorption model for hydrophobic organics on natural soils. In the interim the above models can be used to correlate and extend existing data as a means of estimating partial pressures of hydrophobic chemicals sorbed onto surface soils.

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