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ADSORPTION OF VOLATILE ORGANIC CONTAMINANTS ON SOIL AND SOIL CONSTITUENTS

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ABSTRACT

In the past decade, the problem of soil and groundwater contaminations has emerged as a crucial one and has received renewed attention from the scientific community. Although still incomplete, our knowledge of the phenomena governing

the fate and transport of pollutants in the soil environment has improved significantly. One of the most important sub-surface phenomena is adsorption on soil particles. Because adsorption is very much dependent on the type of chemical involved (organic, metal, ionic compound), this review only focuses on the adsorption of volatile organic contaminants on soil and soil constituents. The current understanding and hypotheses pertaining to this subject are discussed for single component adsorption and multicomponent adsorption.

1. INTRODUCTION, SCOPE AND LIMITATION

Currently, a main contamination source for soils is due to the leakage of underground storage tanks (USTs). The United States Environmental Protection Agency (EPA) estimates that at least 25% of the two million USTs existing nationwide represent a potential danger for the environment because of possible leakage[1], and almost all tanks installed prior to 1988 have contamination due to overfills[2]. Thus, not surprisingly, petroleum and refined petroleum products represent today the single largest source of chemical contamination of marine, terrestrial and groundwater environments.[3] These include volatile organic compounds (VOCs) such as low molecular weight aliphatic compounds but also include aromatics such as benzene, ethyl benzene, toluene and xylenes (BTX). Chlorinated hydrocarbons represent an important class of VOCs contaminating the vadose zone from sources such as dry cleaning operations, degreasing in metal industry, paper industry, and pesticide application.

Historically, vapor-phase adsorption and desorption of chemicals on soils and soil constituents has been investigated since at least the early 1920's. The initial studies on water vapor adsorption on soils were made by Thomas[4,5] and Puri et al.[6] who recognized that isotherms were sigmoid-shaped and indicative of physical adsorption and that the amount of water adsorbed was related to the adsorbent's specific surface area. In the 1950's, Orchiston[7] extended the use of the BET theory to water-vapor adsorption isotherms on a number of New Zealand

soils and on clay minerals[8,9,10], obtaining surface areas and an estimate of the packed water molecule's projected area. At the same period, Call[11] investigated adsorption of ethylene dibromide (EDB) on clays. Later, soil scientists initiated studies on adsorption of pesticides and herbicides on agricultural soils[12,13]. It is only recently that, due to the predominance of oil-based contamination, the investigation of the adsorption of petroleum-derived chemicals started.

Environmental pollution is a subject almost without limits and the task of reviewing all the literature on soil adsorption would be too lengthy to be summarized in the given space. Therefore, this review article will concentrate only on the vapor phase adsorption of volatile organic contaminants on soil, with emphasis on the recently published literature.

2. BACKGROUND

Before the review of the literature and discussion of the major findings, one has to be aware of the complexity of adsorption on soils, even though we are limiting it to vapor phase adsorption of VOCs on soil. This complexity is mainly due to the inherent ill-defined nature of the soil and to the large variety and disparity of the chemicals involved. Adsorption, adsorption theories, adsorbents and adsorbates types will be discussed in this first section.

2.1 The adsorption process

Adsorption of gases on solid surfaces has been extensively studied in the literature and numerous monographs reviewed the process[14,15,16]. The *adsorption* process refers to the process where constituents are concentrated at the interface of two phases and is different from the *absorption* process which refers to the process where a component is transferred from the bulk phase of one phase to the bulk phase of another phase. The interaction of contaminant with dry soil should be referred to as adsorption, however, when water is present in the environment

(as soil moisture for example), *absorption* is also likely to take place and the appropriate terminology is *sorption* which includes *adsorption* and *absorption.*

The adsorption phenomena can be due either to physical adsorption or to chemisorption. Physical adsorption involves only weak molecular interactions between the adsorbent and the adsorbate whereas chemisorption involves the formation of a chemical bond between the adsorbate molecule and the surface of the adsorbent[14]. In physical adsorption, no electron transfer or sharing occurs between the adsorbent and the adsorbate and the individuality of the interacting species is maintained. Physical adsorption equilibrium is very rapidly established (except if there are mass transfer limitations in the gas or pore phases) and is reversible. VOCs' adsorption on soil has been shown to be primarily physical adsorption.

Different types of adsorption forces are involved in the physical adsorption process. They can be divided between dispersion-repulsion forces and Coulombic forces. The total dispersion-repulsion energy is also known as the Lennard-Jones 6-12 potential. In addition, if the solid is ionic (e.g. ionic crystal), it will create an external electric field and will induce a dipole in the adsorbate molecule resulting in a polarization energy component. Finally, if the adsorbate molecule possesses a permanent dipole and/or a quadrupole moment, two more contributions to the adsorption energy may arise: the field-dipole energy and the field gradient-quadrupole energy. Kiselev[17] distinguished between "non-specific" adsorption where only dispersion and repulsion forces are present and "specific" adsorption where Coulombic forces are present, although this definition of "specific" and "non-specific" have not been generally adopted in the broader adsorption community. Specific adsorption will not be present if the adsorbate or the adsorbent is non-polar (e.g saturated hydrocarbons; zeolites) but will occur in all other cases. It is therefore clear that, for a given adsorbate, the bond strength will be higher on a more polar surface and, for a given adsorbent, higher for an adsorbate molecule possessing dipole and/or quadrupole moments.

2.2 Adsorption isotherms - Adsorption theories

The *adsorption isotherm* relates the amount of gas adsorbed at equilibrium as a function of pressure, at a fixed temperature. The isotherm characterizes the equilibrium of an adsorbent-adsorbate system and depends on many factors such as the nature of the adsorbate, the composition and pore structure of the adsorbent, and the amount of moisture present. The adsorption isotherm gives quantitative and qualitative information about the interactions existing between the adsorbent and the adsorbate. Its accurate determination and the evaluation of its sensitivity to the mentioned variables is essential.

Various theories have been developed to interpret adsorption data and only an outline will be given here. The theories and models developed to interpret the different types of isotherms are based on three different approaches: the Langmuir kinetic approach, the Gibbs approach and the potential theory. Only the first two are summarized below since these theoretical approaches are the ones used to interpret data on adsorption of VOCs on soil and soil constituents.

2.2.1 Kinetic approach

The derivation of kinetic adsorption isotherms is based on the equality of the forward and reverse adsorption rates. The theoretical equation for monolayer adsorption was derived by Langmuir in 1918[18]. Subsequently, Brunauer and his associates[19] developed the equations for multilayer adsorption and after reviewing literature data on gas adsorption concluded that there exists, for physical adsorption, five types of gas adsorption isotherms[20]. Type I isotherm is the Langmuir isotherm and is characteristic of microporous solids where the number of adsorbed layers is less then one (unimolecular or monolayer adsorption). Isotherms of types II and III refer to adsorption at a free surface or at a quasi free surface in a macroporous solid whereas isotherms of type IV and V refer to

adsorption in mesoporous solids. Isotherms of type IV and V are usually accompanied by capillary condensation and a hysteresis loop. Most experimental data on adsorption of VOC vapors on soil exhibit the BET Type II behavior[11,21,22,23,24,25,26,27,28].

The BET theory is based on the assumption that multimolecular adsorption is caused by the same forces that produce condensation. For multilayer adsorption with no limitation on the number of adsorbed layers, the isotherm functionality is[19].

$$\frac{y}{X(1-y)} = \frac{c-1}{X_m c} y + \frac{1}{X_m c} \qquad (1)$$

where y is the relative vapor concentration P/P_0, X_m is the monolayer adsorption capacity, that is the amount of contaminant needed to complete the monolayer coverage per unit mass of adsorbent, and c is the BET constant. This is the so called two parameter BET equation and is applicable in the range $0.05 \leq y \leq 0.30$. Recognizing that the number of adsorbed layers is usually limited enabled Brunauer et al.[20] to develop an isotherm equation valid for the whole range of relative vapor pressures. This equation is known as the BET three-parameter equation or the BDDT equation[20]:

$$\frac{X}{X_m} = \frac{cy}{1-y} \frac{1-(n+1)y^n + ny^{n+1}}{1+(c-1)y - cy^{n+1}} \qquad (2)$$

The parameter n is the theoretical number of adsorbed layers. In practice, both equations (1) and (2) yield similar values for X_m and c, however, analysis of the experimental data using equation (2) is more accurate since it takes into account the isotherm in the entire range of relative vapor concentrations. In addition, equation (2) is actually valid for both type II and type III isotherms.

Useful information can be extracted from the BET analysis of the isotherms. The BET constant c is related to the net molar heat of adsorption ΔH_s by the equation[20]:

$$- \ln c \simeq \frac{\Delta H_s + \Delta H_v}{RT} \quad (3)$$

where R is the gas constant, T is the system temperature, and ΔH_v is the partial molar enthalpy of vaporization. Evaluation of the heat of adsorption is important in discriminating between physisorption and chemisorption and in assessing the strength of the adsorption. Physical adsorption is similar to condensation, i.e. the heat of adsorption is somewhat greater then the latent heat of condensation, 40-50 MJ/kmol (~9.5-12 kcal/mol), whereas the heat of adsorption for chemisorption is more like the heat of a chemical reaction, ~200 MJ/kmol.

The value of X_m enables the calculation of the surface area, S_m, covered by an unimolecular layer of the adsorbate using the equation:[29]

$$S_m = \left(\frac{X_m N_o}{M}\right) \alpha \quad (4)$$

where N_o is the Avogadro's number, M is the molecular weight of the adsorbate and α is the area covered by one adsorbed molecule. Although there is some uncertainty in the calculation of α, especially for multi-atom molecules[30,31], it is generally agreed that α is the projected area of an adsorbed molecule on the surface when the molecules are arranged in close two-dimensional hexagonal packing. If the adsorbing molecules are assumed to be spherical, α is then given by[29]:

$$\alpha = 1.091 \left(\frac{M}{N_o \rho}\right)^{2/3} \quad (5)$$

where ρ is the density of the adsorbed molecule in the liquid state at the adsorption conditions. The surface area calculated through organic adsorption can be compared with the BET surface area determined by nitrogen adsorption at 77K and gives insight on availability of adsorption sites.

2.2.2 Gibbs approach

Isotherms derived from this theory are based on the Gibbs equation and on an equation of state for the adsorbed phase[32]. The Gibbs equation relates the spreading pressure π and the number of moles in the adsorbed phase n_s as:

$$A\left(\frac{\partial \pi}{\partial P}\right) = \frac{R\ T}{P}\ n_s \qquad (6)$$

where A is the surface area, T the temperature and P the pressure of the vapor. Since π is not a measurable quantity, an equation of state has to be assumed for its calculation. By analogy with gas phase equations of state, adsorbed state equations of state relate the spreading pressure (equivalent to pressure) to the area occupied by one molecule (equivalent to molar volume) and to the temperature. Each equation of state leads to a different isotherm.

2.2.3 Adsorption on Soil

VOCs adsorption on soil is almost exclusively interpreted by BET isotherms by all investigators in this area. BET theory is routinely used for determination of surface areas of catalysts and other adsorbents, in fact nitrogen adsorption at 77 K is the standard method used to report surface areas. However, the fact that an equation fits the experimental data does not prove that the theoretical approach is sound. Proven usefulness of the BET equation in surface area measurement should not mask the fact that it relies on several unsound and crude assumptions. Its disregard of surface heterogeneities [the BET theory relies for the first layer on a constant heat of adsorption independent of the extent of coverage] might, for example, be crucial when considering an adsorbent as heterogeneous as soil. It also assumes that the heat of adsorption is constant for all the succeeding layers which has been proved to be false by Harkins by experimental determination of the heat of desorption of water from anatase[33]. On

the other hand, there is evidence in the literature showing that, although heterogeneity has a large effect at low vapor pressures, its effect decreases as adsorption proceeds and becomes negligible around complete surface coverage[33], which would legitimate surface area calculations by the BET method. Another uncertainty in the application of the BET theory to determine surface areas is linked to the evaluation of the area occupied by one adsorbed molecule. There is evidence in the literature that this area is not constant but depends on the adsorbate[31] and Karnaukhov[31] challenged the use of Equation 5 for adsorbates other than nitrogen. However, it is likely, that the BET theory will remain the theory of choice for adsorption in general, and soil adsorption in particular. In addition, extension of the kinetic theory approach to multicomponent adsorption does not work very well as will be explained later.

2.3 Types of soils and soil constituents

Soil is formed from the constant destruction of rocks as a result of weathering and its formation is affected by numerous factors such as climate, vegetation, parent material (rock from which the soil originates), topography and biotic (organisms). Soil is a complex three-phase system containing a solid part, a gas part (pore space) and a liquid part (pore space filled with water and/or organic liquid). The relative importance of each phase is dependent on the soil environment such as climate, depth, temperature, although all three phases are generally present in the subsurface environment[34]. Because of its porous nature, soil has the ability to adsorb large quantities of VOCs and large amounts of contaminants exist in the soil in the adsorbed phase, which is very much different from a bulk liquid phase. The soil solid phase is a complex and ill-defined matrix. As shown in Figure 1, it is composed of an inorganic part and an organic part. As far as vapor adsorption is concerned, these two categories are essential since they have been shown to behave quite differently. The inorganic phase is itself divided into crystalline and non-crystalline phases.

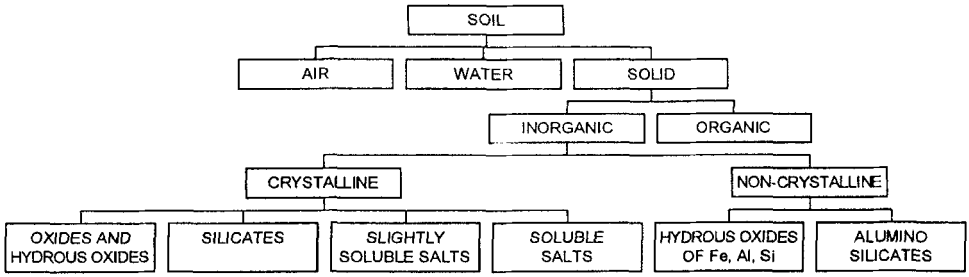

FIGURE 1
Soil constituents (Adapted from Uehara and Gillman[35])

The materials found in the soil solid phase are generally classified according to their size-distribution as clay, silt or sand. The divisions between the fractions are typically made such that clay is less than 2 μm, sand greater than 50 μm, and silt in between. This is not to say that all clay minerals present in a soil are necessarily to be found in the clay fraction, nor silica in the sand, but the division serves as a broad statement of where large concentrations of certain types of soil minerals will be found after gravimetric separation. It does not mean either that soils are composed only of clay minerals (phyllosilicates), sands (silicas), and some intermediate category. Actually the minerals which may be found in soils are much more numerous than just two silicates[36]. For example, iron-oxide minerals such as goethite and lepidocrocite may be found in the clay fraction while not being clay minerals. The above statements are made because there are a few studies in the vapor adsorption literature where sand refers to the particle-size fraction. One such report giving typical surface areas per soil separates is Fuller[37].

Quartz and the disordered polymorphs, crystabolite and opal, are the forms of silica ($Si0_2$) commonly found in the soil environment. Quartz is by far the most prevalent and is the only silica polymorph of concern in adsorption experiments. Quartz is a crystalline material. whose crystals are very close, dense, pure and hard. They are typically large (approximately 100 μm or greater) and have only

little internal porosity and low specific surface area. Therefore, quartz is not a very good adsorbent; however, its abundance is such that it has a definite impact on soil adsorption characteristics and its study is important.

Other important types of crystalline materials are clay and mica minerals which compose a group under the more general class of silicate minerals. They are virtually ubiquitous in soils and often compose 10% to 70% of a soil solid phase. The particle size of clay minerals is often less than 2 μm, and the clay fraction of a soil often holds the large majority of the clay minerals in the soil. The structure of phyllosilicates like clay and mica is that of layers composed of silica tetrahedral sheets and an octahedral sheets, centered around either divalent (commonly Mg^{2+}) or trivalent (commonly Al^{3+}) cations. The repeating unit of the sheets has led to further classification of the clay minerals as either 1:1 (i.e. one tetrahedral and one octahedral sheet) and 2:1 (i.e. tetrahedral-octahedral-tetrahedral sheet arrangement) phyllosilicates. All micaceous substances are 2:1 structures. Some examples of soil clay minerals are kaolinite (a 1:1 structure), smectites (many 2:1 structures including montmorillonite), vermiculite (a 2:1 structure) while some under micas are muscovite and glauconite. Because there is often a net negative charge imbalance within tetrahedral and octahedral sheets in 2:1 minerals, the presence of interlayer cations is required to make up the difference. The cations are often easily exchangeable and allow for many of the unique properties of phyllosilicates. Water is also often present in the interlayer of 2:1 minerals and also occasionally in kaolinite (called in this case halloysite). Some of the adsorptive phenomena that occur with phyllosilicates, such as smectitic swelling in the presence of moisture, are related to the charge distribution of the layers and the kinds and quantities of cations and water present in the interlayer. The implications of these statements with regard to adsorption by phyllosilicates are discussed below.

Soil organic matter (SOM) is the residue from the partial decomposition of cellulose and other natural organic materials in the soil environment. It also is an ill-defined macromolecule, coiled and branched to an overall length of approximately 50 nm and with a molecular weight of approximately 150,000, but

of no definite or commonly agreed molecular formula[38]. Some of the organic groups commonly found in soil organic matter are peptides, sugars, carbazole, maleic, acetic, aliphatic and fatty acids, alkanes and polycyclic aromatics. Such terms as humic and fulvic materials are frequently associated with the term SOM. Humus has no other meaning than SOM which is not recognizable under a light microscope as possessing the cellular organization of plant material[39]. Distinctions between humic and fulvic materials are generally made based upon solubilities at various pH values.

Since it is not a well defined substance, a model is often adopted for SOM. There have been a number of SOM-model substances mentioned in the experimental literature: high-organic-content peat, humic acid, humic-acid coatings, ground cellulose, organic matter chemically recovered from natural soils, fungal melanins and polymaleic acid.

Of the general constituent classes of soil, SOM is recognized as the most important sorbent of nonionic organic chemicals from water. In the frequently moist soil environment the polar water molecules exclude the relatively non-polar organic chemicals from adsorbing to the crystalline mineral surfaces. In contrast, sorption of organic chemicals to the SOM is frequently large. Dissolution of very substantial quantities of organic chemicals in SOM is due to the chemical effects brought about by the combination of polar and non-polar groups forming the SOM. The forces affecting sorption are, then, those of dispersion, polar interaction and hydrogen-bonding.

2.4 Types of adsorbates

The term "volatile organic compounds" includes a large range of chemicals exhibiting widely different physical and chemical characteristics. After reviewing the available literature on organic sorption on soil, Bailey and White[40] showed, that organic sorption is affected by the physical-chemical nature of the adsorbate, the soil organic content, and the moisture content. However, it is reasonable to expect

that only a few of the adsorbate characteristics actually affect and determine its behavior with respect to adsorption on soil. Inspection of the forces responsible for adsorption show that the polarity of the adsorbent and adsorbate will influence the magnitude of the adsorption. There is actually experimental evidence in the literature that polar molecules are more strongly adsorbed than non-polar molecules[41,42,43,44]. Cabbar[42] also showed that apparent exceptions to this rule are due to the existence of two chemical conformations with different polarities for single compounds. In such a case, the magnitude of adsorption is actually linked to the polarity of the most abundant configuration in the gas phase and not to the average polarity of both configurations. However, it appears that polarity is not the only important characteristic and Goss[43] showed that, in regard to adsorption from vapor phase to soil, chemicals are best characterized by their vapor pressures, their polarity and their hydrogen-bonding capacities. Chiou and Kile[44] established that liquid solubilities in soil organic matter (SOM) extrapolated from vapor isotherms were positively correlated with the organic's polar interaction and hydrogen bonding parameters. Typical physical and chemical data for some of the most investigated VOCs are given in Table I. The parameters δ_d, δ_p and δ_h are respectively the dispersion component, the polar component and the hydrogen-bonding component of the total solubility parameter of the organic liquid, δ_0. The magnitude of these components is related to the magnitude of the specific molecular interactions: dispersion force, polar interaction and hydrogen-bonding. The total solubility parameter of the organic liquid, δ_0, is calculated by the equation:

$$\delta_0^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (7)$$

3. SINGLE COMPOUND ADSORPTION ON SOIL AND SOIL CONSTITUENTS

In the past decades, studies reporting on the interactions between soil and organics have been numerous. However, due to the wide variety of adsorbents and

TABLE I

Physical and chemical properties of selected VOCs

[a] From Weast[45]; [b] From Barton[46]

VOC	molecular weight[a]	P_0 (24°C) (mmHg)[a]	dipole[a] moment (Debye)	δ_0[b]	δ_d[b]	δ_p[b]	δ_h[b]
n-hexane	86.17	142.9	0	7.3	7.3	0	0
CCl_4	153.84		0	8.6	8.7	0	0.3
TCE	131.29	71.0		9.3	8.8	1.5	2.6
PCE	165.83		0	9.9	9.3	3.2	1.4
benzene	78.12	87.5	0	9.1	9.0	0	1.0
C_6H_5Cl	112.56	10.7	1.69	9.6	9.3	2.1	1.0
toluene	92.13	27.5	0.36	8.9	8.8	0.7	1.0
acetone	58.08		2.88	9.8	7.6	5.1	3.4
1-propanol	60.11		1.68	12.0	7.8	3.3	8.5
ethanol	46.07	53.3	1.69	13.0	7.7	4.3	9.5
methanol	32.04		1.70	14.5	7.4	6.0	10.9
water	18.02	22.4	1.85	23.4	7.6	7.8	20.7

adsorbates investigated, disparate results have been reported. It is only recently that, based on a classification of adsorbents and adsorbates, a consensus has emerged. A summary of recent studies and the findings is given in Table II and will be detailed hereafter.

3.1 Experimental methods

The experimental methods used to study vapor-phase adsorption on soils can be divided into two broad categories: the static methods and the dynamic

TABLE II
Experimental conditions and findings of selected studies on adsorption of VOCs on soil and soil constituents.

ADSORBATES	ADSORBENT	EXPERIMENTAL METHOD	FINDINGS	REFERENCE
Benzene Trichloroethene Water	Dry Clays: Ca-smectite HDTMA smectite	Static equilibrium apparatus	-For organics: BET Type II isotherms uptake increases as organic content (OC) increases adsorption on rganic matter (OM) function of polarity partitioning in OM -For water: greater uptake on Ca-smectite isotherm becomes linear and uptake decreases as OC increases	Boyd et al.[43]
Monochloroethane 1,2 Dichloroethane 1,1,1 Trichloroethane 1,1,2 Trichloroethane	Afyon soil	Single pellet moment technique (low concentration)	-Adsorption constant increases with contaminant polarity -Heat of adsorption for monochloroethane (-7.9 kcal/mol)	Cabbar et al.[42]
Ethylene Dibromide (Humidity effect)	6 different soils 2 different clays	Vacuum desiccator method	-BET type II isotherms on all adsorbents -EDB uptake decreases as relative humidity (RH) increases except for Ca-Montmorillonite -at low humidities, adsorption on the inside surface area after opening of the clay structure by water molecules Then, competition is favorable to H_20 -Sorption at the water/gas interface	Call[11]
n-Hexane	Bentonite Kaolinite Na montmorillonite Mg montmorillonite 3 synthetic soil mixtures	Static adsorption apparatus	-BET type II isotherms on all adsorbents -Adsorbents surface areas determined by hexane and nitrogen adsorptions are proportional	Campagnolo and Akgerman[28]

TABLE II Continued

Benzene Chlorobenzene m-dichlorobenzene p-dichlorobenzene 1,2,4 trichlorobenzene (Humidity effect)	Dry Woodburn soil (low OM)	Dynamic equilibrium sorption apparatus	-On dry soil, organic uptake increases with polarity -BET type II isotherms - reveal adsorption mainly on mineral matter (MM) -Uptake decreases as RH increases and isotherm becomes type III and linear	Chiou and Shoup[21]
Trichloroethylene Benzene Carbon tetrachloride Water	Peat Muck (High OM content)	Static vapor equilibrium	-For organics: Very linear adsorption isotherms Presence of water does not depress organic adsorption on OM as much as on MM -For water: Same isotherm for both soils although they have different surface areas	Rutherford and Chiou[45]
Water Ethanol Hexane 1,1,1trichloroethane Trichloroethylene Carbon Tetrachloride Tetrachloroethylene 1,2 dibromoethane	Sanhedron soil Humic acid	Static vapor sorption apparatus (microbalance)	-BET type II isotherm for water and 1,1,1 trichloroethane -About linear isotherm for other adsorbates (linearity associated with partitioning on OM); curvature at low partial pressure due to adsorption on MM. -Greater uptake for ethanol - All uptakes given as ml/g are about identical except for H_20 and ethanol	Chiou et al.[25]
n-hexane 1,4 dioxane nitroethane acetone acetonitrile 1-propanol ethanol, methanol	High organic content peat	Static vapor sorption apparatus (microbalance)	-Linear adsorption isotherms -Higher uptakes for polar compounds -Polar interactions and H bonding contribute largely to the solubility in SOM -Solubility in SOM weel correlated to the component solubility parameter	Chiou and Kile[44]
Benzene Trichloroethylene o-xylene	Fine sandy loam	Headspace method	-Isotherms in presence of water show a better fit to Freundlich than BET	English and Loehr[46]

(continued)

TABLE II Continued

Chloroform Trichloroethylene Tetrachloroethylene (100%RH)	Montmorillonite Silica Gel Livermore Sand Livermore clay & silt Santa Clara soil Norwood soil	Equilibration followed by successive purging	-Linear desorption isotherms on water-coated Montmorillonite and Livvermore clay & silt fraction -Other isotherms are Freundlich type -Microporosity-induced non linearity	Farrell and Reinhard[47]
17 volatile and semi-volatile compounds (Humidity effect)	Quartz sand	Pulse chromatographic method (low concentration)	-Measurements at 30, 50 and 70%RH -Linear isotherms (low concentration range) -For non polar compounds, the adsorption coefficient, K, is a decreasing function of the vapor pressure (at fixed RH) -Greater sorption for polar compounds -Inverse exponential dependency of K vs RH if more than one monolayer of water is adsorbed (≈30%RH); due to adsorption at the liquid-gas interface -Importance of hydrogen bonding -Methanol behaves differently	Goss[48]
23 volatile compounds	Clay materials: Ca-kaolinite Na-kaolinite Bentonite	Pulse chromatographic method (low concentration)	-Different behavior for Oxygen-containing compounds due to hydrogen-bonding capabilities -At low RH, organics can access the internal surface area of clays but are blocked by H20 molecules at high RH -Inverse exponential dependency of K vs RH for $40\% \leq RH \leq 80\%$ -For non polar compounds, adsorption at RH under one monolayer of water depends on BET surface area -Ion saturation (C or Na) does not matter for adsorption of non polar compounds; slight effect for polar compounds	Goss[49]
Polar and non polar volatile compounds (Effects of humidity and temperature)	Quartz sand Ca-kaolinite Na-kaolinite Bentonite	Development of model for adsorption	$\ln K = f_1(\ln V_p, \beta) + f_2(\Delta H_c, \beta)(1/T - 1/T0) - f_3(\beta, mR, \mu)(100 - RH)$ $\ln K(100\%RH) = f(\ln V_p, \beta)$	Goss[43]

TABLE II Continued

Trichloroethylene	Morris loam Hardford loam Rhinebeck loam Bandelier tuff Sapsucker soil Gila silt soil Columbus sand	Batch equilibration and headspace analysis method (low concentration)	- Linear isotherm at low concentration -Vapor phase partitioning coefficient for oven-dried is well correlated with the EGME surface area -Vapor phase partitioning coefficient for air-dried soil and at field condition is well correlated with the oganic carbon content -At field condition, two mechanisms: dissolution in adsorbed water and adsorption on solid from the liquid phase	Ong and Lion[50]
Trichloroethylene (Humidity effect)	Alumina Humic coated alumina Ca-Montmorillonite Kaolinite Iron oxide	Batch equilibration and headspace analysis method	-Low concentration, constant adsorption coefficient K at RH and T fixed -Good correlation between K and the BET surface area -Heat of sorption increases as RH increases -Three proposed regions for effect of moisture: → under 1 monolayer of adsorbed water; K decreases with increasing RH; competition between organic and water for adsorption on solid surface → transition region (1 to 5 layers of adsorbed water) → above 5 monolayers of adsorbed water; K increases with increases RH; organic dissolution in adsorbed (liquid) water and adsorption at the gas-liquid interface	Ong and Lion[51]
p-xylene Water (Humidity effect)	Webster soil Webster HP soil Kaolinite Silica gel	Flow equilibration apparatus (+Methanol extraction)	-BET type II isotherm on all adsorbents -All p-xylene isotherms on different adsorbents coalesce if normalized by the amount adsorbed at monolayer -Non polar compounds have greater affinity for MM than soil OM -Polar molecules can access clay internal surface areas -p-xylene uptake decreases as RH increases -Isotherm becomes type III at high RH	Pennell et al.[26]

(continued)

TABLE II Continued

p-xylene Water (Humidity effect)	Ca-Kaolinite Na-Kaolinite Li-Kaolinite	Flow equilibration apparatus (+Methanol extraction)	-BET type II isotherms for water and p-xylene on all adsorbents -Highest water and p-xylene uptakes on Ca-Kaolinite, lowest on Li-Kaolinite -p-xylene uptake decreases as RH increases -Binary adsorption modeling	Pennell et al.[52]
Trichloroethylene	Humic-coated alumina	Headspace batch equili-bration procedure	-Adsorption coefficients on oven-dry and moist soils much higher than on saturated soil	Peterson et al.[53]
Benzene Dichloropropane Methylcyclohexane Ethyl ether Methanol	Silty loam (Parsons soil) Silty clay loam (Summit and Weller soils) Sandy loam (Bernow soil)	Adsorption chamber	- BET Type II or III isotherms for all compounds except methylcyclohexane (Type I or II) -Soil with largest clay content and surface area (resp. lowest) has the largest (resp. lowest) adsorption uptake -Adsorption dominated by mineral matter, occurs mostly on external surface area -Higher uptakes for polar molecules, especially those with hydrogen bonding potential -Heats of adsorption between 7.8 and 10.5 kcal/mol	Poe et al.[54]
p-xylene Trichloroethylene Toluene Ethylbenzene o-xylene Cyclohexane	Kaolin Webster soil Oldsmar soil Lula (aquifer material) Montmorillonite	Flow equilibration method Headspace analysis method	-BET type II isotherms on anhydrous sorbents -All p-xylene isotherms on different adsorbents coalesce if normalized by the amount adsorbed at monolayer (identical for TCE) -Linear isotherms for adsorption on air-dry sorbents (>50%RH) - Uptake on air-dry sorbents are 3 order of magnitude lower than on anhydrous sorbents -Isotherms are almost independent of temperature when plotted as a function of relative pressure ($\Delta H_{ads} \approx \Delta H_{vap}$)	Rao et al.[55]

TABLE II Continued

Toluene p-xylene Ethylbenzene Water	Bentonite Kaolin Webster soil Oldsmar soil Lula Silica Gel	Flow equilibration apparatus (+Methanol extraction and gravimetric measurement)	-BET type II isotherms on all adsorbents except for alkylbenzene on Oldsmar soil and water on bentonite - Bentonite and soils adsorbed much more water than alkylbenzene - Kaolin adsorbed about equal amounts of alkylbenzene and water -Silica gel adsorbed twice as much alkylbenzene as water -Dry MM has good organic adsorption capacity	Rhue et al.[56]
p-xylene (Effects of salt - $CaCl_2$- and humidity)	Webster soil Webster HP (after OC removal) Sand fraction of Oldsmar soil	Flow equilibration method (+Methanol extraction) Pulse gas chromatography	-BET type II isotherms on Webster, Webster HP, sand and salt treated sand at 0%RH -BET type III isotherms at 90% RH -greater adsorption on Webster HP than Webster (more MM exposed) -Presence of salt reduces adsorption at 0 and 90% RH (reversible effect) -Adsorption on hydrated quartz sand occurs primarily at the gas-liquid interface	Rhue et al.[27]
Benzene Dichloromethane	Auberry Sandy Loam Kettleman Hills soil	Static sorption chamber	-BET type II isotherms on air dry soils and at 25% RH -greater sorption on Kettleman Hills soil due to greater surface area	Shonnard et al.[57]
Trichloroethene	Soil from Picatinny Arsenal (NJ)	Static sorption chamber	-BET type II isotherms for water and TCE at 0% RH, greater water adsorption -TCE isotherm becomes type III as RH increases, uptake decreases -In the field, TCE concentration in gas phase increases linearly with distance from the land surface (temperature effect) -field uptakes are 1 to 3 orders of magnitude higher than that estimated from the organic-soil-water isotherm possibly due to slow desorption mechanism	Smith et al.[58]

(continued)

TABLE II Continued

Pentane Trichloroethylene Tetrachloroethylene 1,1,1 Trichloroethane 1,1,2,2 Tetrachloro - ethane Benzene, Toluene Ethylbenzene Acetonitrile Acetone Diethylether (Effect of humidity)	Calcareous soil from Southern Nevada -medium to fine sand and clay size fractions	Inverse gas chromatography	-Slow (limiting) desorption rate for organic on dry soil -For non hydrogen bonding compounds, linear isotherms in presence of water at low concentration, no kinetic rate limitation -For hydrogen bond accepting VOCs infinitely soluble in water, there exists kinetic limitation -Heat of sorption at 52%RH around -10 kcal/mol -At 52%RH, the adsorption coefficient for sand fraction is well correlated to the adsorption coefficient on the clay and silt fraction supporting the hypothesis of a similar adsorption mechanism.	Steinberg and Kreamer[59]
Methylene chloride Carbon tetrachloride Tetrachloroethylene n-Hexane , Toluene	EPA standard soil	Frontal analysis chromatography	-BET type II isotherms for all organics -Heat of adsorption around (-10) kcal/mol -Two-step desorption: multilayer desorption/monolayer desorption	Thibaud et al.[24]
Chlorobenzene Toluene Water (Humidity effect)	EPA standard soil	Frontal analysis chromatography	-Organic uptake is depressed by the presence of water -Type II isotherm becomes type III isotherm at high RH -Competitive adsorption between organic and water molecules for adsorption sites even at high RH -Desorption is enhanced when moisture is present in the desorption stream	Thibaud et al.[41]

methods. Static methods involve batch experiments where soil and vapor are brought into contact and allowed to equilibrate under carefully monitored conditions. After equilibration, the vapor phase is analyzed usually by gas chromatography and the soil phase uptake is determined. This technique is also called the headspace method[53] and can be used to investigate binary or multicomponent adsorption. The solid phase analysis methods include gravimetric measurements and solvent extraction. Static adsorption experiments have also been conducted by gas expansion methods using commercially available equipment[28]. In this method, the adsorbed amount is directly calculated based on the pressure change in the adsorption chamber. It is therefore not applicable to multicomponent adsorption. Static methods are usually time-consuming since equilibration can typically take days or even weeks. Chiou and Kile[44] reported that batch adsorption experiments for some sorbates, such as vapor phase adsorption on dry peat or SOM, could take up to two to three weeks for a single equilibration. Such a long equilibration time is not only impractical but can also impair the accuracy of the measurement by desorption of water from the walls of the apparatus.

Dynamic methods are mainly chromatographic methods where an adsorbent column is subjected to a pulse or step input of contaminant[24,62]. The response to a pulse input is also known as peak broadening method whereas the response to a step input is known as frontal analysis chromatography. Monitoring of the effluent concentration yields a broadened pulse or a breakthrough curve that can be analyzed to calculate the amount of contaminant adsorbed. These methods have many advantages including speed and versatility and can be used for mixed gas experiments. Desorption profiles can also be obtained by these methods. However, careful attention should be given to the elimination of any possible rate limiting process that could prevent reaching the true thermodynamic equilibrium. In addition, in dynamic response experiments mass transfer parameters can also be determined from the data.

3.2 Experimental findings

In the last decades, research on VOCs adsorption on soil has mainly focused on understanding the mechanisms responsible for adsorption on the various soil constituents and on quantifying the adsorption in terms of available surface area and adsorbate characteristics. Some significant progress has been made and it is now recognized that various soil constituents interact differently with adsorbates. Namely, organic and inorganic surfaces have been shown to exhibit particular sorption characteristics. Details of these properties are given hereafter for minerals surfaces (clay, sand, oxides) and organic matter.

3.2.1 Adsorption on mineral surfaces

3.2.1.1 Clay minerals

Typically, in a moist soil environment clay minerals are not the most important sorbents of organic chemicals among the constituents of soil. The polar water molecules have a greater affinity for the crystalline phyllosilicate surfaces than the typically non-polar organics and coupled with their ability to hydrogen bond, they succeed in excluding organic chemicals. For reasons discussed above, in the presence of moisture the SOM has the greatest specific capacity for organic chemicals. Phyllosilicates in the natural soil environment, however, given that they form a very substantial fraction of the overall soil mass, may in sum retain a significant fraction of the total organic-chemical contamination. This would be especially true in a low- SOM content soil.

Under anhydrous conditions the phyllosilicate minerals generally have the greatest capacity among soil constituents for retention of non-polar and slightly polar organic contaminants. In contrast the SOM in the absence of moisture is not a significant sorbent for non-polar and slightly VOC's while it may be for polar compounds. It is not unusual for 2:1 clay minerals, such as montmorillonite, to

have a maximum adsorption capacity of 200-300 mg VOC adsorbed/g montmorillonites while the 1:1 layer clay, kaolinite, being generally uncharged and have no spacing created by interlayer cations, would have a capacity 1/4 to 1/2 of that. Most frequently the shape of the VOC adsorption isotherm on the anhydrous phyllosilicates is unequivocally of BET Type II shape, indicating monolayer followed by multilayer adsorption. Occasionally, the knee of the isotherm is not very sharp which would indicate that the monolayer is not completed before a secondary layer begins to form. However, the sigmoid shape is usually distinct. The only common condition under which VOC-clay mineral adsorption would assume a BET Type III adsorption shape indicating weak attraction would be in the presence of water vapor competing for the crystalline surface. There are a number of factors affecting single-component adsorption capacity of VOC's by phyllosilicates.

The type of cation present in certain minerals may affect its capacity in a number of ways. Jurinak[63] demonstrated the effect of exchangeable cations on the adsorption of ethylene dibromide (EDB) by a montmorillonite. Starting with a montmorillonite from the same source, he homionically substituted magnesium, calcium and sodium in the mineral's interlayer and examined each for its sorptive properties. The energy of hydration exhibited by the cations and thus the amount of water retained in the interlayer had a profound effect on the mineral's capacity for VOC adsorption. This would be expected for such a highly expandable 2-1 phyllosilicate since the water expands the structure allowing for more surface area for adsorption, i.e expands the layers so that the internal surface becomes accessible. Jurinak[63] observed that the montmorillonite with Mg^{2+} had the greatest capacity with the one with Ca^{2+} second and Na^{+} last. But he showed by normalizing the EDB adsorption isotherms by the BET monolayer adsorption capacity (dividing X by X_m) that the exchangeable cation effect was not purely one of relative increase in surface area since the reduced isotherms did not exactly overlay. He suggested that the secondary effect of the kind of exchangeable cation was related to the magnitude of its bond for the crystalline surface.

The effect of substitution of exchangeable cation on adsorption would be expected to be much less for certain other minerals such as non-expandable 2:1 phyllosilicates (i.e. micas) which have only limited cation exchange capacity (CEC) and kaolinite which regularly has no exchangeable cations at all in its ideal formula. Pennell and co-workers[54] observed virtually no surface area differences when they saturated a kaolinite with calcium, lithium and sodium. The kaolinite would be expected to be virtually unchanged by saturating it with cations. Dixon[64] has mentioned the conditions under which occasional isomorphous substitution could occur in the formation of kaolinite, leading to some CEC, but typical kaolinite CEC is approximately 0 to 10^{-2} mol cation/kg. Hence any cation effect on VOC adsorption is not of much importance.

As mentioned above, the expendability of certain 2:1 layer phyllosilicates has great impact on the VOC adsorption capacity. Certainly retained water in the interlayer is of importance, but the effect of the VOC itself may also have profound effect. For many VOCs which have zero dipole moments (e.g. alkanes and alkenes, tetrahalogenated methanes, benzene) and others which have only low dipole-moment-to-molecular-weight ratio and no ability to hydrogen bond (e.g. toluene, chlorobenzene, alkylbenzenes, chloroform), there will be little if any increase in the surface area (beyond external surface area) due to swelling of the layer structure. The surface areas obtained from VOC/BET analysis will be on the same order of the conventional N_2/BET surface area since the nitrogen is non-polar as well. The effect of some polar VOCs in revealing increased surface area is, however, quite remarkable. It is widely recognized that the adsorption of ethylene glycol (EG) and ethylene glycol mono ethyl ether (EGME) onto expandable smectites reveals BET surface areas perhaps an order of magnitude larger than the conventional N_2/BET value[65]. Thus EG/BET surface areas are sometimes referred to as the "total" estimates. In a recent paper, Chiou et al.[66] have demonstrated the difference in adsorption isotherms between EGME and conventional nitrogen sorbates on Ca-montmorillonite (smectite), illite (mica) and kaolinite. The quantities of polar (EGME) and non-polar (N_2) sorbates uptaken by the expandable

smectite showed the greatest difference. The non-expandable mica and the kaolinite were much less profoundly affected by the polarity of sorbates. The same expansion effects that arise because of retained interlayer water, as seen above, can thus also be induced by the polar organic adsorbate. Where water cannot cause expansion, then neither does the polar organic. As a natural consequence of this observation, it should be then recognized that the adsorption isotherm with water vapor as the adsorbate is likely to be much closer to the EG or EGME isotherms than to that for non-polar VOCs or nitrogen[65].

The ability of an adsorbate to hydrogen bond must also be a factor affecting its adsorption to phyllosilicates. Certainly some part of water adsorption to a mineral surface must be due to hydrogen bonding and some part to expansion of the structure (where possible) although it is not clear if contributions to adsorption more than that obtained from a non-polar, non-hydrogen-bonding sorbate (e.g. nitrogen) can be separated into distinct additions. A few VOC adsorbates have some chemical features similar to water so that there must be some common forces in play when they act as adsorbates. One such VOC is methanol which, like water, has approximately the same dipole moment, low molecular weight, the ability to hydrogen bond and small molecular diameter pointing to equal accessibility in pores. Adsorption isotherms obtained with methanol and similar compounds (such as ethanol or water) do exceed those obtained from non-polar, non-hydrogen-bonding adsorbates and BET surface areas obtained from them exceed the conventional nitrogen BET estimates[24,28]. This tends to support the conclusion that there are other contributions (hydrogen-bonding and expansion of the structure) occurring, but again it cannot be further subdivided.

There is some evidence to suggest that net charge of the phyllosilicate layers also have some effect on the shape of the VOC-on-clay-mineral adsorption. The net charge of 2:1 phyllosilicate minerals are by nature negative which is the reason that interlayer cations are required. The kind and quantities of cations present, their hydration properties and other related characteristics play a role in determining the VOC adsorption capacity as noted above. Since the magnitude and

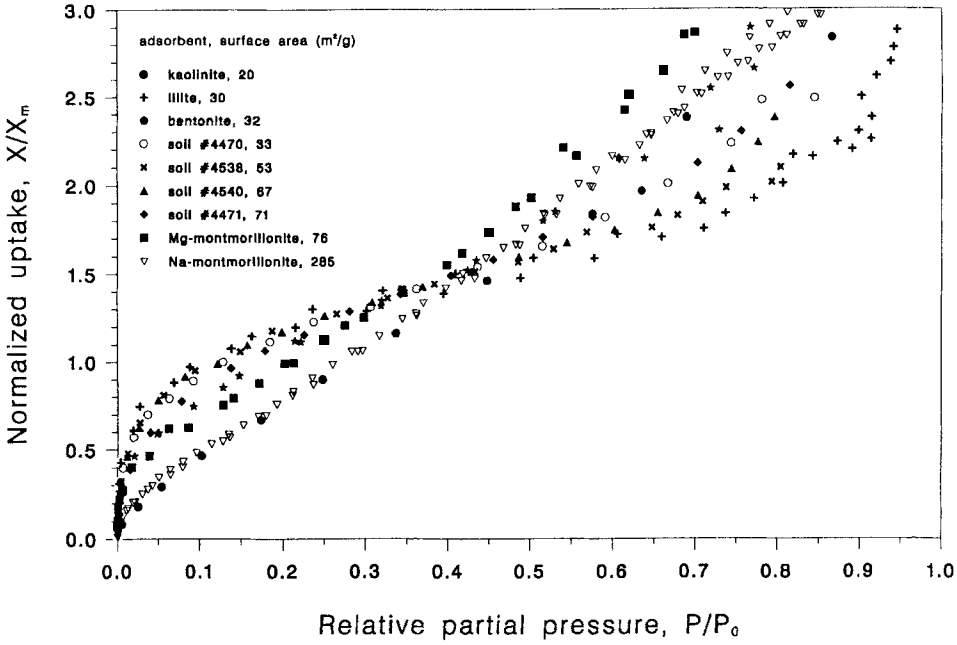

FIGURE 2
Normalized adsorption isotherms of n-hexane on several dry adsorbents at 24°C.

distribution of the charge between the tetrahedral and octahedral sheets also affect swelling ability of the clay mineral, the sheet charges certainly have many fold indirect effects on amounts of VOC adsorption. The evidence displayed in Figure 2, where the adsorbate (*n*-hexane) is fixed while various adsorbents (soils and clay minerals) are compared, is offered to suggest that the net forces of attraction are also affected by net sheet charge[28]. Since the isotherms are reduced by the BET monolayer coverage, the intrinsic differences in surface areas are divided out. The variation in the sharpness of the "knees" of the adsorption isotherms in Figure 2 appears to be related to the charge per formula weight of the clay minerals. For instance, kaolinite having zero charge per formula unit has a comparatively gradual slope (BET c = 6.4) in the initial portion of the isotherm while the clay mineral illite with a charge of 0.6 to 1.0 electrons per formula weight has the most

pronounced knee ($c = 71.4$). The intermediate-charge clays such as montmorillonite (a smectite) and bentonite (a rock term for a mixture of smectites) have isotherms which lie in between the two extremes. The Highbanks soils, being predominantly smectitic and illitic, are likewise intermediate between the two extreme curves. Since the Reagan soils are also of mixed mineralogy with a large illitic fraction, they, while lying within the extremes, are nearer the illite curve. This ordering is reasonable since the effect of the increasing structural charge is to increase the polarization force for non-polar molecules (here n-hexane), and both polarization and other electrostatic forces for molecules with dipole and quadrupole moments. While there are warnings in the literature[67] that the BET c parameter is not an accurate estimator of the actual heats of adsorption, it can be used for qualitative comparison.

3.2.1.2 Quartz

There are a few recent studies which have specifically experimented with quartz at either dry or damp conditions[50,68]. The conclusions to be made from these articles are that:

1) Surface areas from N_2/BET analysis on quartz are approximately 0.1 to 0.3 m^2/g for sands between 30 and 250 mesh. Surface area measurements logically increase slightly with smaller particle size.

2) The quantities of contaminant chemicals adsorbed onto quartz are small. For low values of P/P_0 (i.e. $P/P_0 < 0.10$), a linear adsorption isotherm is justified and describes well the VOC equilibrium between vapor and solid. This holds for dry and moist systems.

3) In the absence of moisture VOC adsorption occurs at the solid surface. With sufficient moisture present to form a layer of sorbed water molecules (generally, the levels of humidity present in ambient air) the VOC sorbs at the liquid-gas interface. At relative humidities above a value that is necessary for the formation of a water monolayer on the quartz surface, an inverse exponential relationship between sorption and relative humidity is observed.

4) The amounts adsorbed are influenced by an adsorbate's ability to form hydrogen bonds.

Besides the above generally qualitiative statements, there has been a recent effort to produce an adsorption prediction method for low concentartion systems of VOCs on quartz and a few other substances. Examining adsorption at varying levels of humidity, Goss[43] correlated the adsorption equilibrium coefficient to temperature by use of the van't Hoff equation. His full correlation for the adsorption coefficient K [= (mg of organic/surface area of sorbent (cm^2))/(mg of organic/volume of gas phase (cm^3))], developed from his very low gas-phase concentration VOC adsorption data on polar mineral surfaces (such as quartz, kaolinite), was recently presented:

$$\ln K = A^* - \frac{\Delta H_s}{R}\left(\frac{1}{T} - \frac{1}{323.15}\right) - C^*(100 - RH) \quad (8)$$

where

$$A^* = -0.615\ lnP_0 + 7.86\ \beta - 5.80 \quad (9)$$

$$\Delta H_s = 3.20\ lnP_0 - 50.2\ \beta - 55.0 \quad (10)$$

$$C^* = -0.054\ \beta - 0.00070\ mR - 0.0041\mu + 0.00061 \quad (11)$$

The correlation's parameters are the vapor pressure P_0, the H-bond acceptor β, the dipole moment μ and the molar refraction mR. The other variables are the molar heat of adsorption ΔH_s, the gas constant R, the temperature T and the relative humidity RH. The correlation is valid for relative humidities greater than 30% and is only applicable to VOC adsorption onto polar sorbents: quartz sand, silica, kaolinite, and a bulk water surface. It is not applicable to bentonite, a rock term

TABLE III

Values of parameters for equations (8-11) for selected VOCs

(Adapted from Goss[43])

VOC	ln P_0 (Pa) @ 25°C	μ (Debye)	mR	β
Benzene	9.45	0.00	26.49	0.10
Toluene	8.25	0.40	31.14	0.11
p-Xylene	7.07	0.10	35.79	0.12
n-Hexane	9.86	0.03	29.94	0.00
Chlorobenzene	7.37	1.60	31.31	0.07
TCE	9.20	0.80	25.32	0.05
Chloroform	10.13	1.10	21.15	0.10

for a mixture of smectites. It is limited to low organic concentrations where the adsorption isotherm can be approximated by a linear functionality. Values of the correlation's parameters for selected VOCs are given in Table III.

Figure 3 shows some typical isotherms for trichloroethylene reported by Steinberg and Kreamer[61] for relative humidities from 1.5 to 15% RH at 40°C. More recently, Kreamer et al.[68] measured the adsorption of trichloroethylene on quartz sands and fitted the experimental adsorption isotherms to the Freundlich equation. However, the exponent of the equation being very close to 1, the isotherms can be considered as essentially linear.

Some single-component VOC-adsorption experiments on silica substances have also been carried out at higher pressures. Ong and Lion[53] used silica (Min-u-sil 5, N_2/BET surface area: 4.9 m^2/g) with trichloroethene (TCE) and water adsorbates, taking 80-90% of the entire adsorption isotherms. These had the Type-

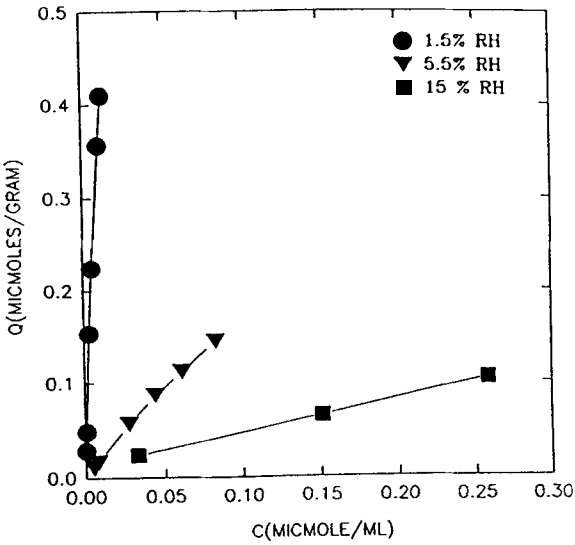

FIGURE 3
Adsorption isotherms of trichloroethylene on sand at 40°C and 1.5, 5.5 and 15% Relative Humidity (Adapted from Steinberg and Kreamer[61])

II shape while displaying low adsorption (< 15 mg/g maximum). Campagnolo and Akgerman[28] also obtained a Type-II isotherm for the adsorption of n-hexane on quartz which had a N_2/BET surface area of 0.5 m^2/g. It is probable, then, that the linear adsorption isotherm model, adequate for low gas-phase concentrations of VOC's, is not so for higher concentrations if high accuracy is required.

The literature on high-surface silica gel and commercial silica powders is substantial and will not be reviewed here since these are more in the industrial-adsorbent/catalysis realm than in the environmental.

3.2.1.3 Other soil minerals

Constituents of soil other than clay minerals (phyllosilicates), quartz and SOM sometimes appear in experimental studies investigating the sorptive

capacities of a range of minerals. Iron oxides (e.g. goethite, hematite, ferrihydrite or models for these), aluminum oxides and hydroxides (e.g. gibbsite, diaspore or models), calcite and other minerals are beginning to receive some attention as adsorbents of organic chemicals. Generally, it appears that iron and aluminum oxides/hydroxides have sorptive capacities on the order of a 1:1 layer phyllosilicate like kaolinite. This is not to suggest that their structures are similar or that the oxides examined were even well crystallized. Chiou and Rutherford[69] have recently examined iron oxides (hematite, synthetic and natural hydrous ferroxides) and aluminum oxide. The hematite was an adsorbent of EGME and nitrogen on the order of sand: BET surface areas of approximately 1 to 2 m^2/g. The other natural iron oxides and aluminum oxide were similar to kaolinite in sorption of EGME and nitrogen. Interestingly, the adsorption isotherms appear to be Type II for both EGME and nitrogen. It is not expected that mineral forms of the oxides would have any swelling capability like expandable 2:1 layer phyllosilicates. There have been a few other recent studies that have included gas-phase adsorption on oxides (e.g. Ong and Lion[70] reported data on Fe_2O_3). Again, the surface area obtained from TCE and water vapor adsorption was similar to that for kaolinite.

3.2.2 Adsorption on soil organic matter (SOM)

The interpretation of how SOM acts as a sorbent is controversial and much of the vapor-phase adsorption literature on it is designed to explore mechanisms. Before 1979, SOM was regarded as a high-surface-area substance. Bower and Gschwend[71] had reported very high surface areas for SOM, 560-800 m^2/g, based on the amount of ethylene glycol (EG) retention data taken at room temperature. The analogy was made between EG uptake by SOM and physical adsorption by clay minerals. From 1979, Chiou and coworkers[21,25,44,47,72,73] have reported evidence which they submit as demonstration that soil SOM functions primarily as a partition medium rather than as an adsorbent in the uptake of (nonionic) organic compounds. Their arguments for the partition model are (1) that the sorption

isotherms for organic solutes (from liquid-solid systems) and organic vapors (from gas-solid) on SOM are linear up to high relative concentrations, (2) that heats of sorption are low, (3) there are no competitive effects between binary solutes, (4) the compliance of sorption data with Flory-Huggins theory, (5) low BET surface areas (approximately 1 m^2/g when measured by conventional N_2 uptake). Chiou and coworkers have argued for what Pennell and Rao[65] have called a "polymer-phase model" where a major amount of the organic chemicals are partitioned by solution into the polymer phase. The high EG/BET surface areas seen for SOM-type materials are thus the result of the polar EG molecules causing polymer swelling and solution.

Chiou and Kile[44] have summarized the limiting partition capacities and the partition solubility of organic chemicals in vapor form for a high-organic-content peat (Table IV). The limiting capacity of the organic matter is obtained by extrapolating the linear adsorption isotherm of the chemical on peat to $P/P_0 = 1.0$ and normalizing the obtained capacity by the mass fraction of organic matter present in the peat. This calculation is valid only if it is assumed that any other matter besides organic matter in the peat is of no importance in adsorption of the chemical. Since the solubility of liquids in an amorphous polymer is better represented in volumetric terms, the authors further define the volume fraction solubility, (Φ^o). The volume fraction solubility in organic matter is obtained by multiplying the limiting partition coefficient (Q^o_{om}) by the dry density of the SOM (assumed to be 1.3 g/ml) and dividing by the liquid density of the organic chemical. The trend of the data apparently shows that organic compounds which involve polar interactions and hydrogen bonding are retained by SOM most readily. The two parameters Φ^o and Q^o_{om} were found to be well correlated with the values of $\delta_p^2+\delta_h^2$ which indicated that adsorption on polar SOM was not affected by dispersion forces.

On the other hand, Pennell and Rao[65] have suggested a "three-dimensional system" model. They note that while Chiou and coworkers have attributed both polar organic and also non-polar organic chemical sorption onto anhydrous SOM

TABLE IV

Limiting Partition Coefficient (Q°_{om}) and Volume Fraction Solubilities (Φ°) of Organic Chemicals in Peat Organic Matter (Adapted from Chiou and Kile[44])

Volatile Organic Compound	Q°_{om} (mg/g)	Φ°
n-hexane	28.2	0.053
carbon tetrachloride	65.9	0.051
benzene	38.9	0.054
trichloroethylene (TCE)	80.0	0.067
1,4-dioxane	80.2	0.092
ethylene glycol monoethyl ether	190	0.21
acetone	171	0.22
nitroethane	272	0.25
acetonitrile	344	0.36
1-propanol	313	0.34
ethanol	396	0.40
methanol	620	0.51
water	370	0.33

to partitioning, there is evidence to suppose that the non-polar organic vapors adsorb in the same manner as N_2 molecules. Thus, non-polar VOCs such as *p*-xylene, toluene, ethylene dibromide and *n*-hexane, yield about the same anhydrous-SOM surface areas as that for conventional N_2/BET analysis, typically ~ 1 m^2/g. On the other hand, BET analysis of the uptake of polar organic molecules, such as EG and EGME, yield surface areas on the order of that for water adsorption. The strength of the interaction is related to adsorbate polarity.

Thus, they concluded that the magnitude of the adsorbate-adsorbent interactions, and not the molecular size, determines the degree to which the

adsorbate explores the internal surface area of the dry SOM adsorbent. Pennell and Rao assert that the interlamellar swelling which polar adsorbate molecules induce when adsorbing to expandable smectite clays, solvating with exchangeable cations associated with the internal surfaces, has an analogue in the effects that they produce when exposed to anhydrous SOM. Similarly, non-polar VOCs and nitrogen are restricted to adsorption to the external surfaces of clay minerals and SOM alike. Furthermore, the authors state that VOC adsorption isotherms on SOM materials give evidence of being either BET Type II or Type III, and that while the low gas-phase concentration portion of the isotherm may appear linear, there is no theoretical justification to take this as vapor-phase partitioning into the SOM. The three-dimensional system model, offered by Pennell and Rao, proposes that SOM contains a multi-polymer phase in a semistructured framework. This phase possesses an internal porosity, which may expand and contract depending on solvent properties. When the multi-polymer phase is air-dried, the surface polar functional groups orient themselves toward the interior of the SOM structure and the external surface becomes primarily hydrophobic. Under anhydrous conditions, the non-polar vapors condense on the external surface. Polar vapors cause opening up of the structure and exposure of the internal surfaces and solvation with associated cations, just as occurs with expandable phyllosilicate minerals. Under saturated conditions, the multi-polymer phase functions as a conventional partition medium for nonionic organic compounds.

There is some independent experimental evidence to support the assertions of Pennell and Rao that non-polar VOC adsorption onto anhydrous SOM is BET Type III and that when moisture, either in the form of water vapor or liquid, begins to saturate humic matter the sorption isotherm resembles linear partitioning. Ong and Lion[70] in studying the adsorption of TCE onto humic acid demonstrated that the anhydrous material adsorbs in a Type III shape with a maximum of 50 mg/g being achievable at $P/P_0 = 1.0$. At 80% RH, there is a many fold jump in the gas-phase quantities that can be sorbed into the humic acid and the isotherm appears linear, but not conclusively so. Apparently, the retention is much more

than can be uptaken even in the aqueous-solution system. However, it should be noted that the VOC isotherms are essentially linear between P/P_0 of 0-0.5 and in type III isotherms the upward concavity starts at P/P_0=0. Never-the-less this is a controversial issue and researchers do use both models.

Apart from its role as a sorbent, SOM also has another effect on sorption by soils. The chemical and mechanical action of water movement and weathering smears SOM over the surfaces of soil minerals, occluding some fraction from organic adsorbates. In the presence of water, the mineral surfaces would adsorb little in any case. Under dry conditions, however, the minerals are the primary adsorbents. Treatment by hydrogen peroxide to reduce SOM from a soil and subsequent re-measurement of its anhydrous adsorption isotherm using a non-polar vapor tends to produce a higher specific surface area for that soil[11]. This tends to support the occlusion theory. Campagnolo and Akgerman[28] showed that occlusion is primarily due to weathering under moist conditions and not just simple mechanical action by demonstrating that after mixing and light grinding of sand, clay mineral and SOM constituents without wetting, the mixture isotherms for N_2 and *n*-hexane could still be predicted entirely from the weight fractions of constituents and the pure component isotherms.

A few conclusions can be made from the examination of vapor-phase sorption of organic-chemical vapors to SOM model substances:

1) SOM is a very important sorbent in a natural, moist soil environment, but it is not a strong adsorbent of non-polar and slightly polar chemicals as its typical specific external areas of just ~ 1 m^2/g from N_2/BET and many organic/BET experiments suggest. Its potential for the uptake of polar organic molecules is very great with EG or EGME surface areas measuring 500 to 800 m^2/g. The mechanism of sorption, whether it behaves as a polymer partition medium or as a potentially swelling adsorbent, is controversial.

2) Weathering of soil causes to some degree the smearing of SOM over mineral surfaces. This may have the effect of occluding mineral surfaces from potential adsorbates and reducing the amount of adsorption per gram of soil. This

may be especially important under dry conditions where minerals are the strongest adsorbing constituents of soil.

3) Quantities sorbed increase with the polarity of the sorbate due to increased polar forces, and polar compounds with the ability to hydrogen bond are sorbed in the greatest quantities. In contrast, non-polar substances are not sorbed in large amounts. As an example of the amounts to be expected of each, the following amounts were obtained for sorption on dry peat by Chiou and Kile[44] at P/P_0 = 0.30, methanol (150 mg/g or 4.69 mmol/g), ethanol (110 mg/g or 2.39 mmol/g), acetone (40 mg/g or 0.69 mmol/g), *n*-hexane (10 mg/g or 0.11 mmol/g).

4) A linear adsorption isotherm clearly is applicable for adsorption of both polar and non-polar sorbates on SOM substances up to approximately P/P_0 = 0.50. Vapor-phase adsorption of slightly polar and non-polar VOC's on anhydrous SOM model substances, such as humic acid, frequently assume a type III shape or a marginally type II shape, indicating weak interactions with the external surface.

3.2.3 Additivity of dry constituents surface areas

Neglecting the occluding effect of SOM on soil minerals, the single-component VOC adsorption isotherms and dry surface areas of soils may be estimated from the weighted sum of those for the individual constituents[74] and where the VOC is non-polar the phyllosilicate minerals (and other clay fraction minerals) composing the soil will account for most of the total surface area[28]. Also, soils originating from the same area but coming from different horizons and having different mass fractions in the clay fraction can be scaled to match each others based upon the relative clay fractions as can be seen from Table V.

3.2.4 Generalization of adsorption isotherms (Kinetic approach)

One of the most important goals of studies of organic adsorption on soil is to develop a methodology to estimate, *a-priori*, the magnitude of adsorption, with

TABLE V

Additivity of dry constituents specific surface areas in a mixture.
(Adapted from Campagnolo and Akgerman[28])

Soil Constituent	weight %	Pure constituents BET surface areas (m^2/g) measured with different adsorbates	
		Adsorbate: Hexane	Adsorbate: N_2
Montmorillonite	25.0	207.1	285.1
Cellulose	6.7	1.9	0.4
Humic Acid	0.3	1.6	0.8
Sand	68.0	0.1	0.5
Mixture surface area : Predicted		(51.9)	(71.6)
Measured		(52.1)	(66.7)

only limited data on adsorbent and adsorbate. The development of such a technique has to be based on experimental findings and theoretical knowledge. As a first step towards an unified theory, several researchers showed that isotherms of different adsorbates on the same adsorbent could be collapsed into a single isotherm when the mass adsorbed is normalized by dividing it by mass adsorbed at monolayer coverage, X/X_m, and plotting the data versus the relative vapor pressure[26,28,57,58,75]. The quantity X/X_m is sometimes referred to as the statistical number of adsorbed layers. Figures 4 through 8 show the reduction of the adsorption isotherms of different adsorbates on one adsorbent and of one adsorbate on different adsorbents (Figures 7,8 and 2).

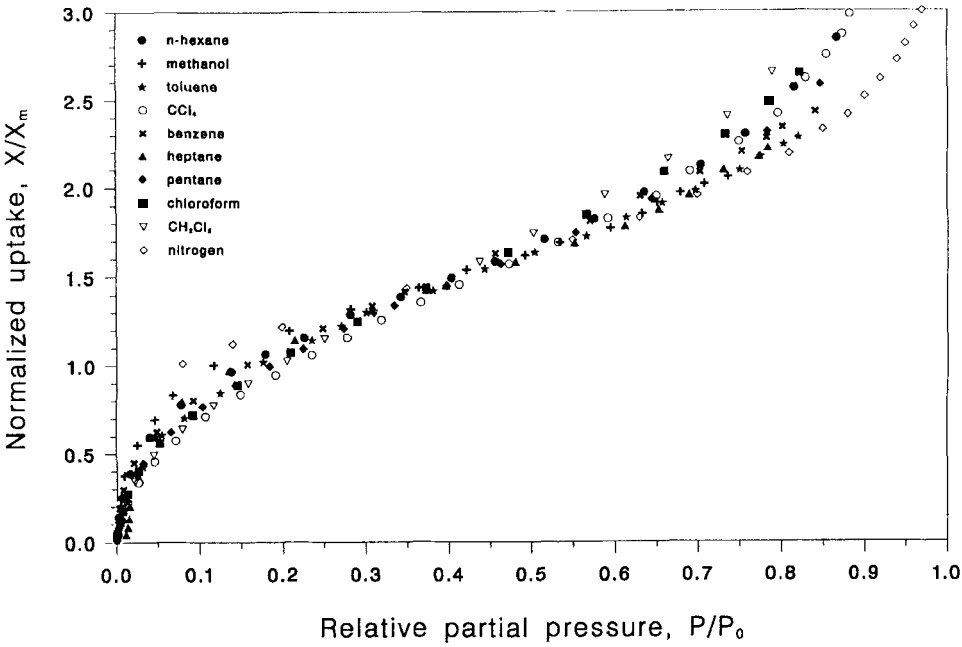

FIGURE 4
Normalized adsorption isotherms of various VOCs on dry Highbanks A soil at 24°C (Adapted from Campagnolo and Akgerman[28])

3.2.5 Prediction method for isotherms

As mentioned above, the adsorption isotherms of various adsorbates on various adsorbents collapsed when plotted in terms of the normalized uptake, X/X_m, versus the relative vapor pressure, P/P_s. Furthermore, Campagnolo and Akgerman[28] noted that, notwithstanding the scattering of the experimental points around the collapsed curve, all the reduced isotherms for a given adsorbent cross at approximately P/P_0=0.4. Identically, the reduced adsorption isotherms of hexane on various sorbents (Figure 2) cross at the point $P/P_0 \approx 0.4$. The significance of this pivot point is not quite understood yet. However, it is worth noting that there is

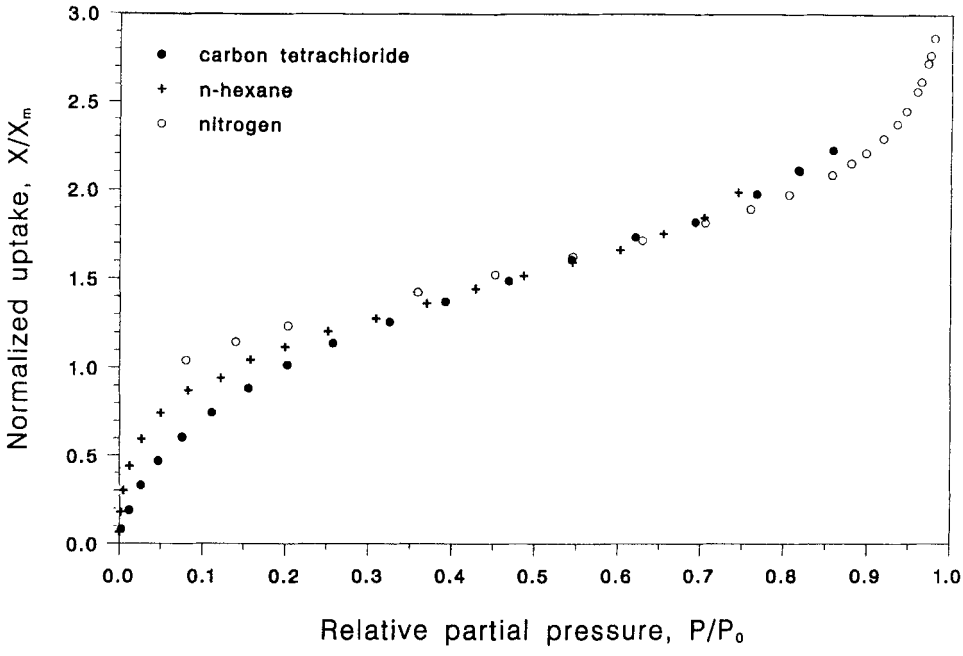

FIGURE 5
Normalized adsorption isotherms of various VOCs on dry Reagan B soil at 24°C (Adapted from Campagnolo and Akgerman[28])

some evidence in the literature linking the point P/P_0=0.4 to the lower closure point of the hysteresis loop of nitrogen at 77 K[76]. The existence, for a given adsorbate at a given temperature, of a point below which the lower closure point of the hysteresis is never situated has been linked to the tensile strength of the liquid adsorbate[77,78,79]. The relative vapor pressure, $(P/P_0)_h$ corresponding to this point would be given by the equation[80]:

$$\ln\left(\frac{P}{P_0}\right)_h = -\frac{V_L}{RT}\tau_0 \qquad (12)$$

where V_L is the molar volume of the liquid adsorbate and τ_0 is the tensile strength

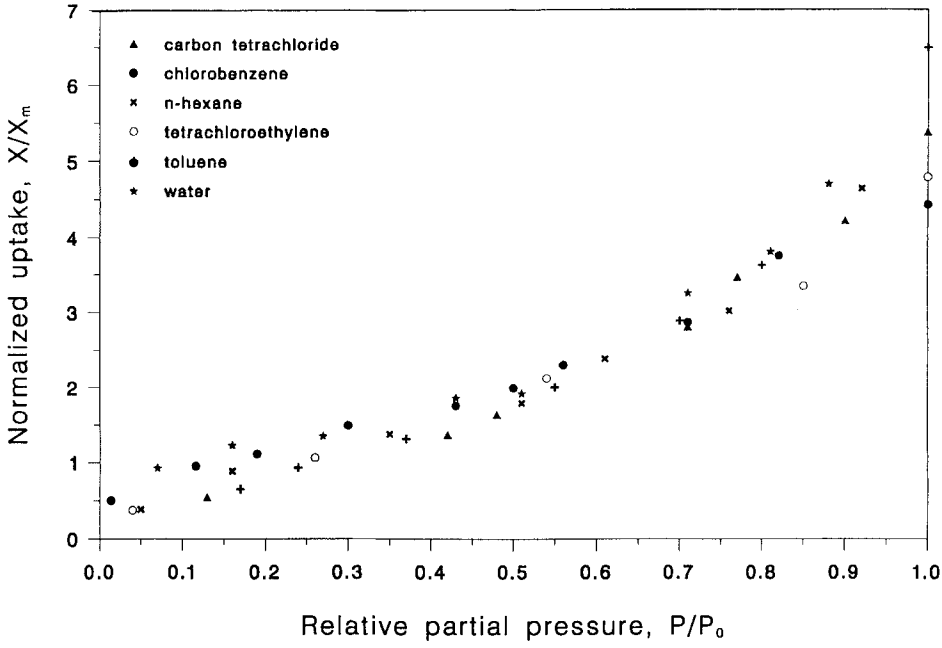

FIGURE 6
Normalized adsorption isotherms of various VOCs on dry EPA soil at 24°C
(Adapted from Thibaud[75])

of the adsorbate. Observed values for $(P/P_0)_h$ are characteristic of the adsorbate but do not depend on the adsorbent. Gregg and Sing[80] summarized some observed values and gave a value of 0.42 for nitrogen at 77 K, 0.17-0.19 for benzene at 298 K, 0.20-0.25 for carbon tetrachloride at 298 K and 0.50 for butane at 273K.

If, as indicated by all the data in this study, the value of X/X_m at $P/P_0 = 0.4$ (denoted by $Q_{0.4}$) is the same value for a natural adsorbent over a broad range of VOC adsorbates, then the relation between the BET c and the theoretical number of layers, n, is established by use of the three-parameter BET or BDDT model as:

$$(0.4)^n\left(n + \frac{5}{3} - Q_{0.4}\right) = \frac{5}{3}\left(1 - \frac{3}{5}Q_{0.4} - \frac{9}{10}\frac{Q_{0.4}}{c}\right) \qquad (13)$$

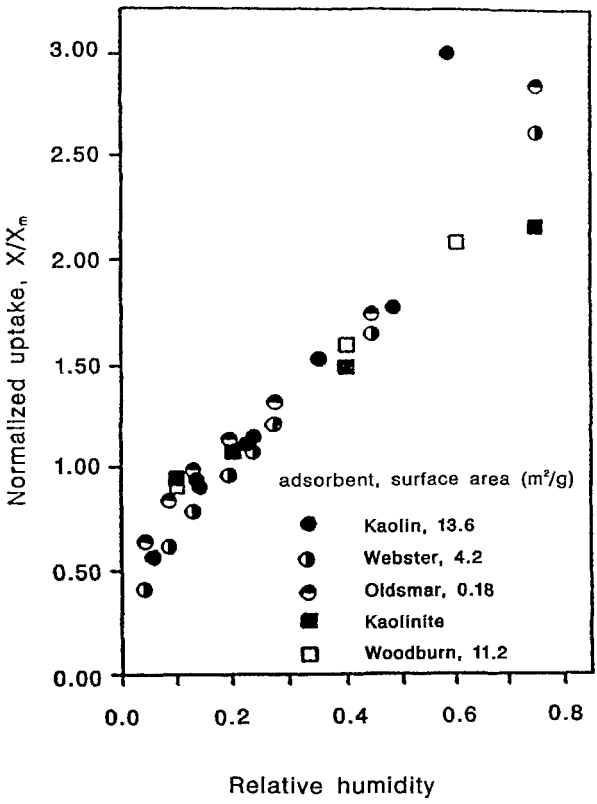

FIGURE 7
Normalized adsorption isotherms of water on various adsorbates (Adapted from Rhue et al.[58])

As implied by this equation, if the BET *c* parameter can be calculated, the number of layers n can be calculated from the above equation. An estimate of the BET *c* 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 the data are for the same adsorbent. For adsorption onto a common adsorbent, Barrer[81], working with zeolites, and Kiselev[82] with carbon black, demonstrated that the

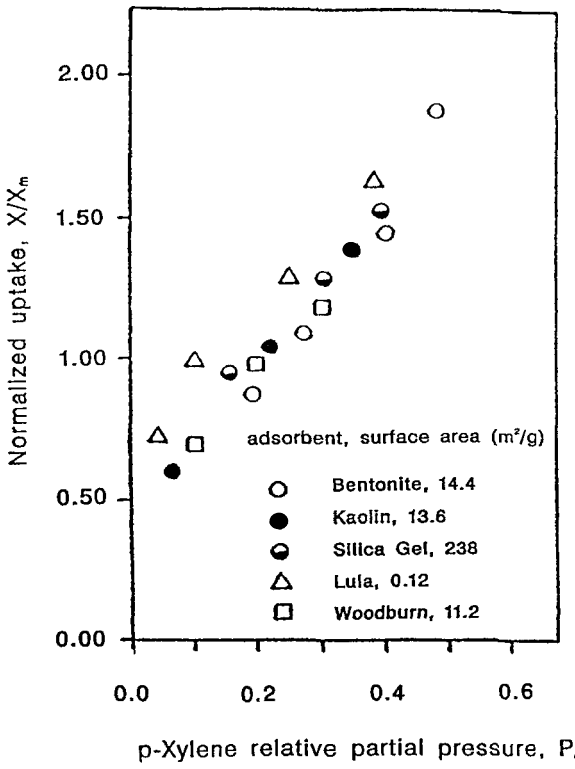

FIGURE 8
Normalized adsorption isotherms of p-xylene on various adsorbates (Adapted from Rhue et al.[58])

isosteric heat of adsorption of alkanes and alkenes vary generally as smooth curves with the number of carbon atoms. Similarly, Campagnolo and Akgerman[28] showed that the variation in heat of adsorption as determined from BET analysis for near members of the homologous alkane series follow a smooth curve. Generally, as a first approximation, it can be assumed that near members of a non-polar homologous series will have the same BET c value.

The means of obtaining the parameter X_m is based upon an observation of Campagnolo and Akgerman[28], and supported by subsequent data. For non-polar

VOC adsorption onto a soil or soil clay mineral at 24°C, it was found that the BET surface area was approximately 0.73 times that of the standard N_2/BET value (at the boiling point of that adsorbate). Thus, the standard surface area in conjunction with the hexagonal closest-packing estimate (Equation 5) in accordance with equation 4 can be used to compute the VOC unimolecular layer amount:
It should be noted that for polar VOC's, the BET surface area measured from

$$X_{m,VOC} = \left(\frac{0.73\, M S_{m,N_2}}{\alpha_{m,VOC}\, N_0}\right) \qquad \textbf{(14)}$$

VOC adsorption may actually exceed the standard nitrogen BET value since in this case specific electrical forces contribute to adsorption, a phenomenon not present in non-polar adsorption. As shown in Figures 4 and 5, normalized adsorption isotherms of various VOCs and of nitrogen on soil collapse into a single curve. Therefore, Equation 14 combined with standard nitrogen adsorption data would be sufficient to predict adsorption isotherms of VOCs on soil. A comparison of the predicted versus empirical monolayer amounts obtained for the adsorbent/adsorbate pairs given in Table VI is given in Figure 9. This prediction method seems to be limited to relatively non-polar VOC's i.e organic chemicals with zero dipole moment (e.g. *n*-hexane, carbon tetrachloride) or with low dipole moments (e.g. toluene). Among polar molecules, the prediction method did work for chloroform but not for methanol. The polar/non-polar distinction is supported by the fact that adsorption of non-polar molecules involve primarily non-specific forces of physical adsorption (dispersion and repulsion). On the other hand, the adsorption of polar molecules onto ionic surfaces, (e.g minerals) commonly involves non-specific and specific forces, and is often dominated by specific electric forces (dipole, quadrupole, adsorbate-adsorbate interactions). Still, a large number of the common contaminants from fuels and solvents belong to the non-polar classification.

TABLE VI

Adsorbent/adsorbate pairs shown in Figure 9.

Point number	Adsorbent	Adsorbate	Point number	Adsorbent	Adsorbate
1	kaolin	hexane	11	HighbanksA	toluene
2	illite	hexane	12	HighbanksA	benzene
3	bentonite	hexane	13	HighbanksB	CCl_4
4	HighbanksB	hexane	14	ReaganB	CCl_4
5	ReaganB	hexane	15	HighbanksA	CH_2Cl_2
6	HighbanksA	pentane	16	ReaganA	CCl_4
7	ReaganA	hexane	17	HighbanksA	$CHCl_3$
8	Mg-montm.	hexane	18	HighbanksA	CCl_4
9	HighbanksA	hexane	19	Mg-montm.	CCl_4
10	HighbanksA	heptane	20	Na-montm.	hexane

4. MULTICOMPONENT ADSORPTION

Although adsorption of a single compound on soil is already a complex phenomenon, it does not give an accurate representation of subsurface contamination since, in the subsurface environment, several contaminants are likely to coexist and compete, and moisture and/or liquid water are likely to be present leading to a multicomponent adsorption situation that is far more complicated and far less understood.

Before developing on the limited available soil studies, we will first summarize the relevant knowledge developed on multicomponent adsorption of gases since there are undeniable similarities between gas adsorption as a unit

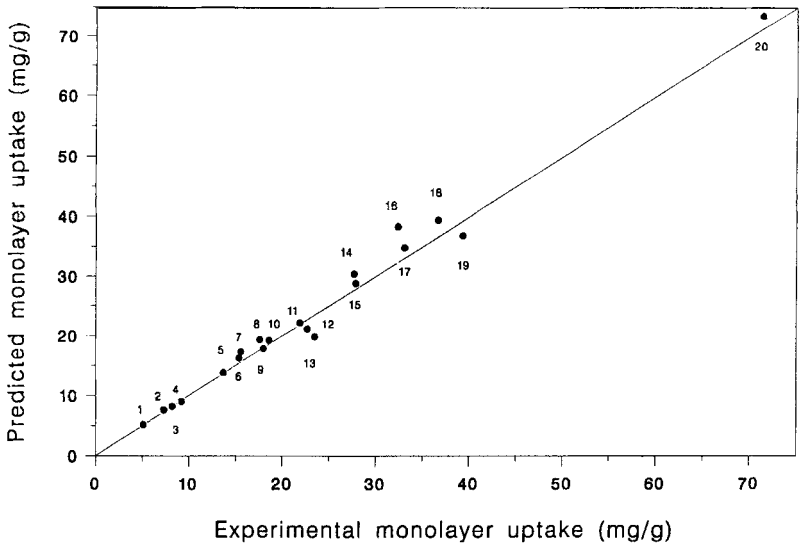

FIGURE 9
Experimental versus predicted uptake at monolayer for adsorbent/adsorbate pairs shown in Table VI.

operation and adsorption on soil matrices. However, one has to beware that gas adsorption as a unit operation is nevertheless different from adsorption on soil in many ways. One essential difference is due to the physical state of the adsorbate which is usually above its critical point in gas adsorption and usually under its vaporization pressure and temperature in soil adsorption. This creates a potential condensation (possibly capillary condensation) problem and an added difficulty due to the addition of one additional separate phase. The other main difference is related to the adsorbent characteristics. Adsorbents for gas adsorption are usually well-defined matrices such as zeolites or activated carbon, whereas adsorbents for soil adsorption are complicated and ill-defined matrices leading to possible multilayer adsorption and capillary condensation. Basically, VOCs adsorption in the moist subsurface can be described as adsorption of immiscible components at conditions below their boiling point and vapor pressure on a heterogeneous matrix.

4.1 Theories on Multicomponent Adsorption

Adsorption of an organic in presence of water or of another organic in the vapor phase is basically multicomponent adsorption. Although numerous theories have been developed to model adsorption of gas mixtures, none of them has been extensively tested for multicomponent adsorption on soil because of the limited data available in the literature.

All classical single-gas theories have been extended to mixtures. Markham and Benton[83] derived the Langmuir isotherm for n-component mixtures and the Freundlich isotherm for binary mixture has been developed by Glueckauf[84]. Those two models are applicable only to monolayer adsorption and are therefore of little use for adsorption on soil. For multilayer adsorption, the BET isotherm has been extended to mixture adsorption by several authors. Hill[85] proposed an equation for n-component adsorption that was simplified by Thibodeaux et al.[86] for the adsorption of semivolatile organic chemicals and by Gu[87] for adsorption of mixed vapors of immiscible liquids. Gonzalez and Holland[88] also proposed a simplified version of the BET model for mixture adsorption and applied it to mixtures of paraffins on activated carbon and silica gel. For multilayer adsorption of gases on relatively non-polar adsorbents, a potential-theory approach has proven more useful than a kinetic-theory approach. Bering et al.[89] extended the Dubinin-Radushkevich equation[90] to adsorption of mixed gases and it has been shown that coupling this equation with the Lewis equation[91] enabled good predictions of binary adsorption of gases[92]. However, two conditions have to be met for the Lewis equation to hold, that is (a) gases are adsorbed by micropore filling, and (b) the adsorbed solution is ideal. While these conditions are probably valid for adsorption of gases with no strong interactions on activated carbon or zeolites, they are very plausible for co-adsorption of VOCs and/or water on soil and soil constituents. When the Lewis rule does not hold, an alternate supplementary equation can be obtained by assuming that Raoult's law applies. Different methods were developed using this assumption and the Dubinin equipotential theory[89] with varying success.[92]

As an extension of the Gibbs approach to multicomponent adsorption, Myers and Prausnitz[93] applied the fundamental thermodynamic equations for liquids to adsorbed gases and developed the Ideal Adsorbed Solution (IAS) theory. The IAS theory is based on Raoult's law and assumes the equality of the spreading pressure for each adsorbed compound. This is the most tested theory for mixture adsorption of gases and it gave good predictions for adsorption on activated carbon[93]. The agreement is not as good for some other cases.[94]

Although, the ideality of the adsorbed solution is usually assumed in all the thermodynamics models, some models have been developed for non-ideal solutions[95,96]. Attempts have been made to predict deviation from ideality and activity coefficients of mixed adsorbed species based on bulk solution theories[96]. However, it has been shown that non-ideal solution in the bulk liquid phase might lead to ideal adsorbed solution[97] and Myers[98] suggested that non-ideality might be only an artifact due to surface heterogeneity.

4.2 Types of adsorbates pairs

Numerous multicomponent studies addressing the simultaneous adsorption of water and organics on soil have been published to this date[26,27,41,50,51,54,99] and numerous researchers recognized the strong competition between water and organic molecules. Goss[43,50,51] studied the effect of relative humidity on the adsorption of polar and non-polar organics in the Henry's law region and concluded that the adsorption coefficient was essentially a function of the compound's polarity and vapor pressure. Steinberg and Kreamer[61] emphasized the importance of the hydrogen bonding capabilities and solubility. However, simultaneous adsorption of organics has not yet received adequate interest and only a few studies report data on this subject. Guo[100] reported data on binary adsorptions of toluene/hexane, toluene/methanol, and chlorobenzene/methanol mixtures on soil and Amali et al.[101] reported data on ternary adsorption of trichloroethylene, toluene and water on sand and silt loam. As already mentioned, the polarity of the adsorbates is an important

characteristic with respect to the extent of adsorption on soil and soil constituents. Identically, it is logical to expect binary adsorption to be at least partly governed by the relative polarities of the adsorbates involved. It should be noted that the binary systems used by Guo are miscible in their liquid state which is not the case for binary adsorption of water and a VOC.

4.3 Adsorption in presence of water - Moisture effect

Beginning in the 1940's, interest in the diffusion of fumigants and pesticides through soils led to the study of the adsorption of these chemicals on soils as a factor affecting their transport. Chisolm and Koblitsky[102] found that methyl bromide adsorption decreased with increasing soil water content. Some fumigants were extensively studied, such as ethylene dibromide (EDB). The studies of Hanson and Nex[103] and of Wade[104,105] with EDB had findings similar to Chisolm and Koblitsky with methyl bromide noting that EDB attraction to the soil is reduced by displacing water molecules, i.e. a transition from Type II to Type III isotherm with increasing humidity. Numerous studies showed that the presence of water depresses the organic adsorption on soil. Call[11] studied the sorption of EDB on moist soils at various levels of relative humidity. He showed that the water vapor displaced the EDB molecules and suggested that EDB sorption on soils in the field was due mainly to solution in the soil water and at the water interfaces. He showed that BET surface areas from water adsorption were well in excess of those obtained from the areas obtained by the conventional nitrogen adsorption (at 77.4 K) and from EDB adsorption, an effect of water's ability to swell expendable phyllosilicates and of hydrogen bonding. He also suggested that SOM occluded the mineral surfaces from serving as adsorbent sites.

Several studies indicated that in presence of moisture organic sorption on soil dramatically decreases[21,26,41,42]. It has been widely speculated that the mineral surface contributes to soil sorption of non-polar organic vapors only at low relative humidity and that, at high relative humidity, the whole available surface is wetted

by water. Therefore, water molecules would preferentially adsorb onto mineral surfaces, thus displacing the organic molecules from the surface[41,52,53]. This argument is supported by the fact that the organic vapor uptake on soils decreases as the relative humidity increases. However, Thibaud et al.[41] showed that, even at high relative humidity levels, adsorption of organic vapors (toluene and chlorobenzene) on soil directly from the vapor phase was significant. Their data show that at low partial pressures of chlorobenzene or toluene, increased humidity clearly decreases the amount of organic adsorbed, however at high partial pressures of the organics (partial pressures in excess of 50% of the vapor pressure) there is significant organic adsorption on the soil surface indicating competitive adsorption (Figure 10). Other investigators also proposed the existence of exposed mineral surfaces even at high relative humidities[26,106]. Conversely, Rhue[99] showed that the adsorption of water on silica gel and kaolin was only very slightly affected by the presence of p-xylene.

Ong and Lion[53] showed that the adsorption reduction versus moisture content curve exhibited a minimum as expected following Hill's theory[83] and its subsequent development by Thibodeaux et al.[84], however, recent experimental data refuted this theory[26,43,44]. Goss[43] evaluated the influence of relative humidity on the sorption of 17 volatile organics on quartz sand at very low organic concentrations and showed that sorption decreased monotonously with increasing relative humidity. Identical results were reported later for sorption on clay minerals[44]. Rhue et al.[99] investigated the effect of water on alkylbenzene adsorption on mineral surfaces and obtained linear isotherms at high relative humidities. As the investigated adsorbents had very low organic contents, they concluded, as did Mingelgrin and Gerstl[107], that linear isotherms were not necessarily due to partitioning. Farrell and Reinhard[49] speculated that linear isotherms are obtained for adsorption on homogeneous surfaces. As already mentioned, Goss[43] used all the available data on organic adsorption on polar mineral surfaces to develop an empirical predictive model for adsorption in presence of moisture and concluded that the important organic properties in evaluating adsorption on polar mineral

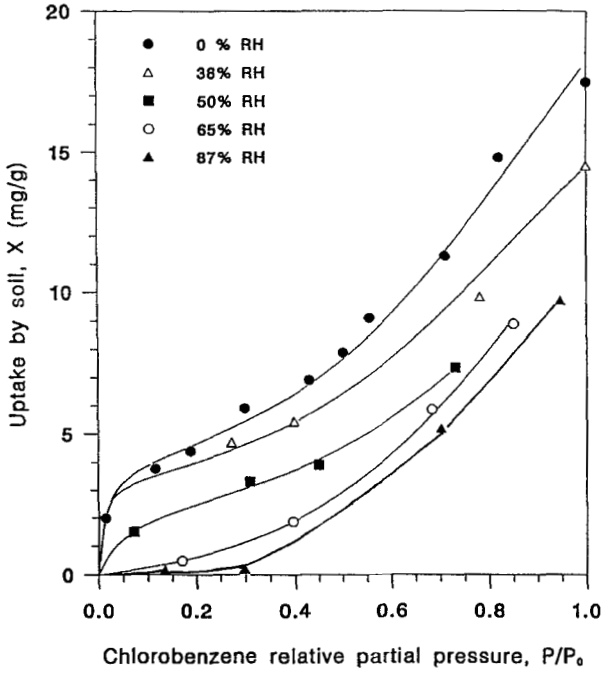

FIGURE 10
Binary adsorption of water and chlorobenzene on EPA dry soil at 24°C: chlorobenzene adsorption isotherms at various relative humidities (Adapted from Thibaud[75])

surface are the vapor pressure and the hydrogen bond acceptor parameter. Unfortunately, this study is limited to low organic relative vapor pressures since it assumes a linear adsorption coefficient.

Vapor-phase adsorption of organic chemicals on SOM in the presence of humidity differs, from that on clay mineral adsorbents. Water vapor tends to facilitate sorption of organic chemicals on SOM by causing the opening of the structure so that either more adsorption sites become available or solution partitioning can occur in a greater volume. Water vapor enhances the SOM capacity for organics. In contrast, the quantities of non-polar VOC adsorbed by

clay minerals is reduced as relative humidity increases and BET Type II isotherms become Type III at high relative humidities. The polar water molecules having a higher affinity for the crystalline clay mineral surfaces tend to displace the relatively non-polar VOC's. Thus, even though polar water molecules expand smectite layers exposing large internal surface areas, VOC's still cannot adsorb in greater quantities.

Few attempts have been made to use kinetic models to predict water-organic adsorption data[23,26,41,99] and none has been successful over a wide range of relative partial pressures. Acceptable prediction results have been obtained at low vapor pressures[26,41] where competitive adsorption is unlikely, but Thibodeaux and Valsaraj[23] found that theoretical models consistently underpredicted the experimental relative partial pressure. The theoretical models developed by Valsaraj and Thibodeaux[23] considered three levels of soil humidity. "Dry" soil refers to soil an amount of water that is less than monolayer coverage (0 to 2% by weight), "damp" soil refers to soil with a water content roughly correponding to monolayer coverage (2 to 4% by weight) and "wet" soil refers to soil with a water content exceeding monolayer coverage.

The cause for the failures of prediction models might lie in the special role of water and in the existence of an adsorbed water phase exhibiting liquid-like characteristics. It is now recognized that, in presence of water, the organic sorption might occur through any of the following processes[26,41]: (a) adsorption onto the mineral surface from the gas phase by competition with water molecules for adsorption sites (gas-solid interface), (b) adsorption onto the mineral surface through the adsorbed water phase (liquid-solid interface), (c) dissolution into organic matter from the gas phase, (d) dissolution into organic matter through the adsorbed water phase, (e) adsorption onto the surface of an adsorbed water film (gas-liquid interface), (f) dissolution into adsorbed water. Each of those phenomenon should be considered if a mechanistic model is to be developed for adsorption in presence of moisture. There are contradictory views in the literature as to which of these mechanisms dominates the sorption of VOCs on soils in the

presence of moisture. Recently, Pennell et al.[26] showed that sorption at the gas-liquid interface for sorption of p-xylene on soil as a function of RH could account for up to 50% of total organic sorption across the whole relative vapor concentration range of the organic. Thibaud et al.[41] found that adsorption onto the mineral surface directly from the gas phase by competition with water molecules for adsorption sites was significant even at high relative humidities and was at all conditions one of the main contributions with adsorption at the gas-liquid interface.

4.4 Binary adsorption of organics

Only recently have researchers begun to study binary adsorption of two organics. As is the case for water and as demonstrated for gas adsorption, it is likely that the presence of two adsorbates will influence the individual adsorption capacity of each adsorbate.

Amali et al.[101] investigated the adsorption of trichloroethylene, toluene and water mixtures on sand and silt. They concluded that there was no competition between TCE and toluene at low relative vapor pressures. Guo[100] studied the binary adsorption of toluene-*n*-hexane, toluene-methanol and chlorobenzene-methanol mixtures on soil using the frontal analysis chromatography technique described by Thibaud et al.[41] for binary adsorption of water and toluene. Experimental results are shown in Figure 11 as percent reduction in adsorption versus relative vapor pressure of adsorbate for the binary systems described in Table VII. The percent reduction due to co-adsorbate effect, η, is defined as:

$$\eta = \frac{X\,[P_1 = x; P_2 = 0] - X[P_1 = x; P_2 = y]}{X\,[P_1 = x; P_2 = 0]} \times 100 \qquad \textbf{(15)}$$

where P_1 is the partial pressure of the adsorbate and P_2 is the partial pressure of the co-adsorbate. The uptake for adsorption of pure adsorbate 1 (denominator of Equation 15) is calculated using the BET parameters obtained by Guo[100] for the

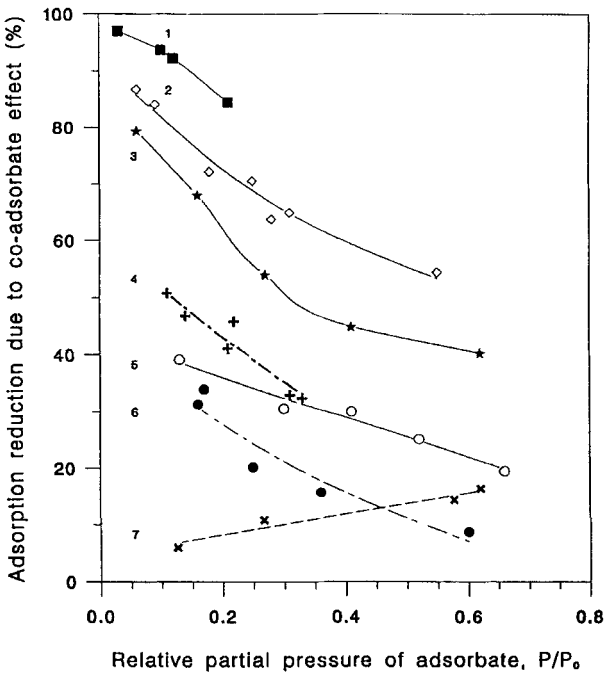

FIGURE 11
Adsorption reduction due to co-adsorbate effect for VOCs pairs described in Table VII (Lines are for eye-guiding purposes only)

pure adsorption isotherm of adsorbate 1. As shown in Figure 11, in all cases, the presence of a co-adsorbate inhibits the adsorbate sorption. The adsorption reduction is percentage-wise more drastic (a) at low partial pressure of the adsorbate (except for methanol, Curve 7), and (b) at high partial pressure of the co-adsorbate (compare curves 1 and 3 and, 4 and 6). From comparison of curves 1 and 4, it can be seen that at equivalent co-adsorbate partial pressures, the presence of methanol reduced the adsorption of toluene on soil much more drastically than the presence of n-hexane. This shows that highly polar methanol molecules appear to compete more effectively with non-polar toluene molecules for adsorption sites than non-polar hexane molecules do. Similarly, the presence of toluene affects only slightly

TABLE VII

Organic pairs and co-adsorbate partial pressure for experimental data shown in Figure 11. (Adapted from Guo[100])

Line number	Adsorbate	Co-adsorbate	Partial pressure co-adsorbate, P_2 (atm)
1	toluene	methanol	0.111
2	chlorobenzene	methanol	0.079
3	toluene	methanol	0.043
4	toluene	n-hexane	0.119
5	chlorobenzene	methanol	0.027
6	toluene	n-hexane	0.024
7	methanol	toluene	0.010

the adsorption of methanol (Curve 7). However, it appears that polarity is not the only important characteristic when it comes to competitive adsorption since, although chlorobenzene and methanol exhibit similar polarities (dipole moments of respectively 1.69 and 1.7 debyes), the reduction in chlorobenzene adsorption due to the presence of methanol is essentially identical to the toluene reduction when the difference in methanol partial pressure is considered. In other words, non polar toluene molecules and polar chlorobenzene molecules exhibit comparable behaviors in presence of methanol.

It also has to be noted that the adsorption of methanol in presence of toluene is more significantly reduced at high relative partial pressure methanol (Curve 7) whereas, for all other pairs, reduction is percentage wise more important at low partial pressures. This shows that toluene competes effectively with methanol at high methanol adsorption but cannot compete at low methanol

adsorption. This could be due to the hydrogen bonding capabilities of methanol that enables it to initially adsorb on sites unaccessible to toluene molecules that do not possess hydrogen bonding capabilities. As the adsorption of methanol increases (i.e. as its relative partial pressure increases), it adsorbs on "regular" sites also accessible to toluene and competition can occur leading to an increased reduction of methanol adsorption.

It has been seen that for single adsorption, hydrogen bonding capabilities, in addition to polarity, influence single vapor phase adsorption of organics on soils. It appears that a similar conclusion is valid for binary adsorption. From Table I, the respective hydrogen bonding parameters of chlorobenzene and methanol are 1.0 and 10.9.

Guo[100] applied the Grant and Manes method[92] and the ideal adsorbed solution theory[93] to predict binary adsorption on soil. The ideal adsorbed solution model well predicted the binary adsorption of toluene and hexane (Figure 12) and the binary adsorptions of toluene and methanol and, chlorobenzene and methanol at low methanol partial pressures. However, the model overpredicted the experimental data at high methanol partial pressures. This failure might be due to the non-ideality of the solution at high methanol partial pressures. Highly non-ideal systems can be described by the vacancy solution theory proposed by Suwanayuen and Danner[108,109]. This method has been shown to work well for adsorption on activated carbon and zeolites. However, it has not been applied to adsorption on soil yet.

5. CONCLUSION

Vapor phase adsorption of VOCs on soil has received increased attention in the past few years. Single compound adsorption on soil and soil constituents has been extensively studied and a common knowledge has emerged. It is now recognized that adsorption of VOCs on soil is due to physical adsorption and can be described using kinetic theories (Langmuir, BET, Freundlich isotherms).

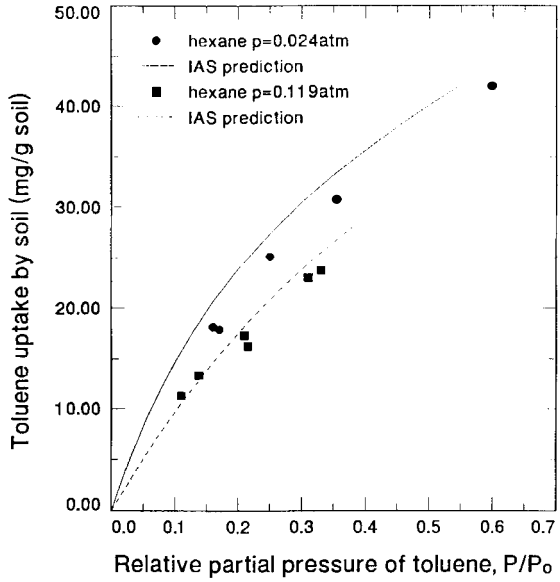

FIGURE 12
Toluene adsorption isotherm and fit by ideal adsorbed solution (IAS) theory for binary adsorption of toluene and n-hexane at two different partial preesures of n-hexane (Adapted from Guo[100])

Adsorption isotherms on dry soil are usually successfully represented by the BDDT equation (equation 2) and it has been shown that the adsorbent surface area as determined by nitrogen adsorption could be used to estimate the adsorption capacity of non-polar and slightly polar compounds. However, polar compounds and especially compounds with hydrogen bonding capabilities have been shown to behave quite differently and to exhibit increased adsorption. This has been linked to the presence of expandable clay materials in the soil matrix.

The understanding of the single compound adsorption is, however, only a first step towards understanding of soil contamination since, at field conditions, it is likely to encounter the simultaneous presence of several contaminants and of water. The study of the effect of water and other VOCs on adsorption of VOCs

is essential in order to achieve a thorough understanding of the phenomena occuring in the subsurface.

Many researchers have shown that the presence of water decreases the adsorption of VOCs on soil and it is hypothesized that the reduction is due to competitive adsorption. Mechanistic models taking into account all the physical phenomena arising from the presence of water molecules (such as adsorption at the gas-liquid interface) have also been developed to model the binary adsorption of water and organics. However, a lot of uncertainty still remains in the understanding of water-organic interactions with respect to adsorption on soil. Finally, the study of binary and multicomponent adsorption of organics on soil is still at its infancy and only a few studies have addressed the problem.

It is the authors' belief that, in order to complete our understanding of the subsurface adsorption phenomena, the adsorption studies in the coming years should focus on binary and multicomponent adsorption of VOCs together with water.

6. NOMENCLATURE

(Note: The number in parentheses gives the number of the equation where the symbol is first used)

A	surface area (6)
A^*	parameter defined in equation (9)
c	BET energy parameter (1)
C^*	parameter defined in equation (11)
K	adsorption coefficient (8)
M	molecular weight (4)
mR	molar refraction (11)
n	third BET parameter (2)
n_s	number of moles adsorbed (6)
N_0	Avogadro number (4)

P organic partial pressure (6)

P_0 organic vapor pressure

Q^o_{om} limiting partition coefficient

R gas constant (3)

RH relative humidity (8)

S_m surface area covered by one monolayer of organic (4)

T temperature (3)

V_L organic molar volume (12)

X organic uptake by the adsorbent (1)

X_m organic uptake at monolayer coverage (1)

y relative partial pressure, P/P_0 (1)

α projected area of an adsorbed molecule (4)

β hydrogen-bond acceptor (9)

δ_0 total solubility parameter (7)

δ_d dispersion component of the solubility parameter (7)

δ_p polar component of the solubility parameter (7)

δ_h hydrogen bonding component of the solubility parameter (7)

ΔH_s molar heat of adsorption (3)

ΔH_v molar heat of vaporization (3)

μ dipole moment

π spreading pressure (6)

ρ liquid density (5)

τ_0 tensile strength of the adsorbate (12)

Φ^o volume fraction solubility

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