# Modeling multicomponent volatile organic and water vapor adsorption on soils

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## Abstract

Volatile organic chemical (VOC) and water vapors are present simultaneously in the soil gas phase. Any modeling of VOC vapor flow must account for the strong competition they experience from water and any competition between themselves. To account for these competitions, the multicomponent form of the Brunauer–Emmett–Teller equation with finite number of adsorption layers was tested. Of the three input constants required in the multicomponent model, two can be obtained from single species adsorption experiments. The third constant was found to be bounded within a fairly narrow range; although its physical meaning is debatable, its value can be approximated fairly accurately. The data used to check the applicability of this model were for the adsorption of trichloroethylene and toluene on a sand and Yolo silt loam (fine-silty, mixed, nonacid, thermic Typic Xerorthent). For relative humidities (RHs) corresponding to less than one molecular layer of water coverage and at low to very low toluene and trichloro ethylene (TCE) vapor pressures, it underpredicted the adsorbed amounts of both species from their binary mixtures with water on both soils. At RHs corresponding to between one and two molecular layers of water coverage, predictions compared well with data. At RHs corresponding to about two layers of water, the model overpredicted the adsorbed amounts. At toluene relative vapor pressures above 0.1 the model reasonably described the adsorbed amount on sand at two RHs corresponding to one to two water layers. This model was further tested on published adsorption data of *para*-xylene and water on soil. It was reasonably successful in describing adsorption of *para*-xylene from its binary mixture with water above *para*-xylene relative vapor pressure of 0.069 and water relative humidity of 0.084. No competition between TCE and toluene was observed at the low vapor pressures in our experiments. Simulations of adsorption in the ternary systems of TCE, toluene, and water followed the same pattern as for the binary simulations.

## 1. Introduction

Realistic modeling of vapor flow for volatile organic chemicals (VOCs), especially in fairly dry soils, requires models of adsorption of these vapors to

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soil particles. The strong competition of polar water with nonpolar VOC molecules for adsorption sites has been recognized by many researchers [1–5]. Under dry conditions, adsorption on the external surfaces of minerals is the primary VOC vapor sorption mechanism [4, 6–9]. The vapor adsorption isotherms on dry soils follow the Brunauer–Emmett–Teller (BET) isotherms [3, 6, 8]. The most observed of the BET isotherms is the Type II which is characteristic of vapor condensation forming multilayer adsorbates on nonporous or macro-porous adsorbents [10]. As the relative humidity (RH) in the soil increases from zero, strong polar interactions between water molecules and soil minerals predominate over the relatively weak Van der Waals forces between the VOC vapor molecules and mineral surfaces [7, 8]. Chiou and Shoup [3] showed that BET adsorption isotherms of a few chlorobenzenes became linear as RH increased to 0.50. Above a RH of 0.50, isotherms became linear for VOC relative vapor pressures (actual vapor pressure/saturated vapor pressure) of less than 0.50. Rhue et al. [9] found that at RH values close to a monolayer of water coverage on a kaolinitic soil and on a silica gel, the adsorption of para-xylene decreased much more noticeably than at lower or higher RH values. At higher RH values, Henry's partitioning into water and partitioning into soil organic matter become the dominant uptake mechanisms for VOC vapors over adsorption on external mineral surfaces [5]. Jurinak and Volman [6] obtained data on adsorption of ethylene dibromide on soils up to a relative vapor pressure of 0.9. They obtained a good fit of the BET equation to the data up to relative vapor pressures of 0.6–0.7. Poe et al. [8] used the BET equation to fit adsorption data of a few widely different chemicals on four types of soils. Their correlation coefficients indicate good fits over the range of data used. The success of the BET equation to fit single vapor adsorption data, particularly in the 0.05–0.3 relative vapor pressure range, has prompted its widespread use in calculations of monolayer coverage and soil surface area from nonpolar compounds (Sing et al. [10]).

Models of multicomponent adsorption must account for the competition of water vapor with the VOC vapors and any competition between the individual VOC vapors. Even though competition between nonpolar VOC species for adsorption sites is expected to be much less intense than competition with water, the strength of competition is expected to increase with the polarity of the species [3, 8]. The extension of the single component multilayer BET isotherm to a multicomponent form presented by Hill [11, 12] may offer some possibilities in this regard. Valsaraj and Thibodeaux [4] used a binary form of Hill's general equation to get simplified isotherms to estimate partial pressures of VOCs above soils. They point out that this equation applies best to results at low VOC relative vapor pressures. Their equation allows an infinite number of adsorption layers thereby assuming that a free liquid surface can be formed on the surface of soil minerals. Thibodeaux et al. [13] used a similar equation to theoretically investigate the adsorption of slightly volatile organic chemical (SVOC) vapors and water on atmospheric aerosols. Their equation indicated the correct behavior of the SVOC isotherm at various RHs. However, the

applicability of their equation to soils is not clear. Rhue et al. [9] proposed a formula for the mass fraction of an adsorbed species in the total mass adsorbed from a binary vapor system. An equation derived based on their equation greatly overpredicts the total mass adsorbed at low water contents but its predictions are reasonably close to measured values at higher RHs. Pennel et al. [14] compared the results of the Valsaraj and Thibodeaux [4] equation and Rhue et al. [9] equation. They collected single and binary adsorption data of *para*-xylene on a kaolinitic soil at low to medium *para*-xylene relative vapor pressure ranges and at RHs corresponding to less than one molecular water layer. The models used in their paper also assume that an infinite number of adsorption layers could form on the surface. They concluded that at low RHs, the binary BET equation underestimated the adsorption of both water and *para*-xylene due to noncomplete monolayer coverage by water. However, it is not known how the BET equation performs at higher RHs and VOC relative vapor pressures.

In this paper we will investigate the applicability of the multicomponent BET model to adsorption of VOC vapors in the presence of water on soils. We will set the maximum number of adsorbed layers ($n$) to be finite and investigate the implications of this choice for multicomponent adsorption modeling. The predictions of the multicomponent BET equation can be compared theoretically against the forms used by Valsaraj and Thibodeaux [4] and Thibodeaux et al. [13], to investigate the possible strengths and limitations of choosing a finite $n$ value. Moreover, we will compare the predictions of the multicomponent BET model with measured trichloro ethylene (TCE) and toluene vapor adsorption data from binary and ternary mixtures with water on a sand and a Yolo silt loam. Finally, we will compare the multicomponent BET model predictions with the results obtained using the equation of Rhue et al. [9] and with their measured data on adsorption of *para*-xylene on Na-saturated kaolin at various water contents.

## 2. Theory

The single species multilayer BET model [15, 16] is based on the following assumptions: (1) energetically and geometrically homogeneous adsorbent surface, (2) no lateral interaction among the adsorbed molecules, (3) adsorption of the molecules of the second and higher adsorbed layers follows the condensation–evaporation properties of the liquid state. Hill [11] assumes the last postulate to be equally applicable to adsorption from a mixed vapor system. Assuming that the adsorbed solution obeys Raoult's law, namely that the mixture of sorbed species behaves as an ideal solution at all compositions, eq. (14) in Hill [11] takes the following form for adsorption of species $i$ from a vapor mixture containing $s$ species,

$$w_i = \frac{w_i^m E_0 x_i}{(1-E) + E_0(1-E^n)} \left[ \frac{B_i(1-E^n)}{E_0} + \sum_{k=2}^{n} E^{k-2}(1-E^{n-k+1}) \right] \tag{1}$$

where $E_0 = \sum_{i=1}^{s} x_i B_i$, $E = \sum_{i=1}^{s} x_i$, $w_i$ is sorbed mass of species $i$ per soil mass, $w_i^m$ is mass of species $i$ required to form a monolayer coverage on adsorbent surface per soil mass, $x_i$ is relative vapor pressure (vapor pressure/saturated vapor pressure), and $B_i$ is related to the molar heat of adsorption of the adsorbate on bare mineral surface [3]. Finally, in eq. (1), $n$ is an integer signifying the maximum possible number of layers of $i$ on the adsorbent surface for single-species systems. In eq. (1) the summation is only taken when $n \geq 2$.

In eq. (1), the assumption of ideality leads to the simplified form of the parameter $E$. However, one would expect eq. (1) to be less applicable to sparingly soluble compounds than to more soluble ones. Furthermore, the applicability range would be expected to be restricted to lower VOC relative vapor pressures.

All the various forms of the BET equation presented in the literature are simplifications of the general multicomponent BET (MBET) form. When considering adsorption of a single species and $n = \infty$, eq. (1) reduces in a linear form to

$$\frac{x_i}{w_i(1-x_i)} = \frac{1}{w_i^m B_i} + \frac{(B_i - 1) x_i}{w_i^m B_i} \tag{2}$$

This form is applied to $0.05 \leq x_i \leq 0.3$ to obtain $w_i^m$, $B_i$, and adsorbent surface area [10]. For single species adsorption and finite $n$, eq. (1) gives the form used by Jurinak and Volman (1957) and Poe et al. (1988) to fit adsorption data of single species of VOC vapors on dry soils. When applied to a binary vapor system and $n = \infty$, it furnishes the form used by Valsaraj and Thibodeaux [4], Thibodeaux et al. [13], and Pennell et al. [14]. When $n = 1$ (i.e., adsorption is restricted to a monolayer), the single species form of eq. (1) reduces correctly to a Langmuir type equation.

The effect of the parameters $B$ and $n$ on the shape of eq. (1) for adsorption of a hypothetical VOC species on dry soils is plotted in Fig. 1. As $B$ increases, a 'knee' is formed at the lower $x_i$ values and $w/w_i^m$ increases to give a sharp drop to zero. The point where the knee occurs is often taken to indicate the stage at which monolayer coverage is complete and multilayer adsorption is about to begin [10, 17]. As $n$ increases, higher adsorption is predicted at higher $x_i$ values until for $n = \infty$, $w_i \rightarrow 1$ as $x_i \rightarrow 1$. As $x_i$ decreases, the difference in adsorption between isotherms for various values of $n$ also decreases. This shows that the choice of $n = \infty$ in the MBET equation may be appropriate in modeling multi-component adsorption at low VOC relative vapor pressures but leads to gross overestimation of adsorption capacity at high relative vapor pressures. Even though the BET theory does not provide a physical basis for why the number of layers should be restricted to a finite value, the presence of capillaries in soils is possibly one cause of this [17]. Fig. 1 indicates that proper choice of $n$ and $B$ may allow various isotherms to be fitted if the monolayer capacity $w_i^m$ is known. In binary form, eq. (1) can be used to look at the effect of increasing RH on the shape of the isotherm and strength of adsorption for a given VOC on
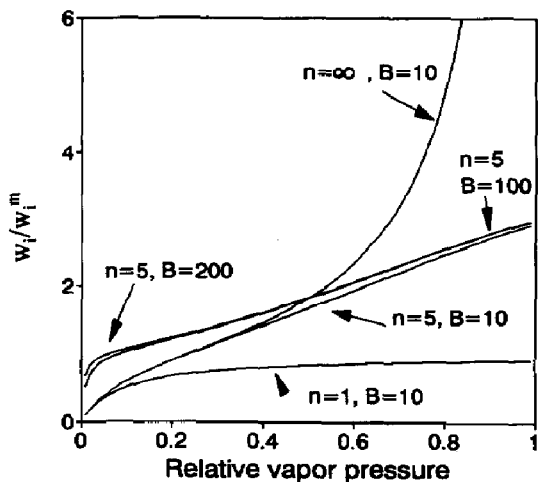
Fig. 1. The effect of $B$ and $n$ on the shape of eq. (1) applied to a single vapor system.
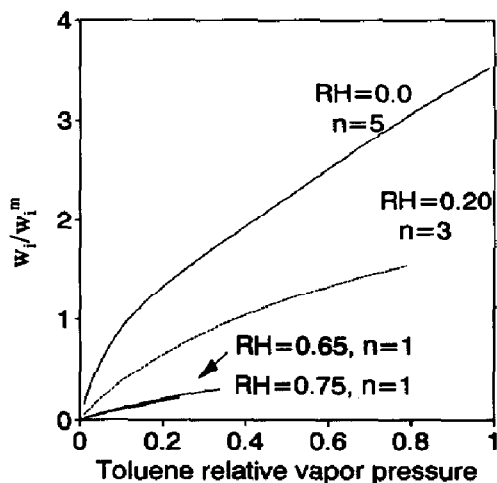


Fig. 2. Effect of water relative vapor pressure (RH) on MBET isotherms of toluene adsorption on Yolo silt loam at 25 °C.

soil. Fig. 2 illustrates theoretical isotherms for toluene on Yolo silt loam at various RH values. The major effects are a linearization of the isotherm with an accompanying reduction in adsorption amounts as RH increases. These effects have been experimentally documented by Chiou and Shoup [3], Rao et al. [18], and Rhue et al. [9], among others.

Rhue et al. [9] presented equations similar to BET which could be used to quantify competitive adsorption in a binary system. Their derivation assumes that the two adsorbates form immiscible films on the adsorbent surface. This assumption is opposite to what is used in deriving eq. (1) which requires the adsorbates to form an ideal solution on the adsorbent surface. When $S_0$ (bare

mineral surface) in their equations is substituted by the external surface area for their soil (given in their paper), their equations lead to an expression giving the mass of a given compound in the total mass adsorbed from a binary vapor system. The final equation obtained is

$$w_i = \alpha_i B_i S_{ext} \frac{x_i}{(1-x_i)^2} \tag{3}$$

where $\alpha_i$ is the mass of adsorbate $i$ occupying unit area of surface and is given by Rhue et al. [9] to be 0.50 mg/m² for para-xylene, $S_{ext}$ is the soil specific external surface area (m²/g), and additional parameters have previously been defined.

The parameter $n$ in eq. (1), when applied to single species adsorption, signifies the maximum number of adsorption layers. However, in a multicomponent situation, the physical meaning of $n$ requires further investigation. A first hypothesis is that as in a single species system, $n$ in a multispecies system refers to the maximum number of layers of the multispecies adsorbate. A second hypothesis is that $n$ refers to an 'equivalent' maximum number of layers of species $i$ on the surface of a soil–water adsorbent complex. We will look at which of these hypothesis may better explain the data.

## 3. Materials and methods

Adsorption was measured on a coarse riverbed sand and Yolo silt loam (fine-silty, mixed, non-acid, thermic Typic Xerorthent). Some relevant characteristics of the two soils are given in Table 1. Total surface areas were determined by the ethylene glycol monoethyl ether (EGME) method [19, 20]. Pretreatment to remove organic matter and saturation with $Ca^{2+}$ were omitted [21]. The organic carbon content of the soils was analyzed by a modified Walkley and Black method [22]. The pH was measured in a saturated paste by pH electrode, while electrical

TABLE 1

Characteristics of the soils used in adsorption experiments

| Characteristic | Riverbed sand | Yolo silt loam |
|---|---|---|
| EGME surface area (m²/g) | 18.7 | 80.6 |
| Organic carbon (%) | <0.1 | 1.05 |
| pH | 8.2 | 7.9 |
| EC (milli mho/cm) | 0.36 | 0.77 |
| CEC (meq/100 g) | 2.3 | 21.1 |
| Sand (%) | 94 | 33 |
| Silt (%) | 4 | 49 |
| Clay (%) | 2 | 18 |

conductivity (EC) of saturation extracts was measured using a platinized plati-num–iridium conductivity electrode and a conductance–resistance meter. Cation exchange capacities (CECs) were determined by saturation with barium acetate [23]. Particle size analysis to determine sand, silt, and clay fractions was per-formed by hydrometer [24]. Initially the soils were air dried, passed through a 2.0-mm sieve (No. 10), and mixed thoroughly to obtain a homogeneous mixture.

To obtain adsorption data in the very low relative vapor pressure range, the equilibrium partitioning in closed systems (EPICS) method [5, 25] was used. The method can briefly be described as a mass balance technique that involves measurement of the headspace vapor concentration in sealed glass bottles by gas chromatography. A system with known gas volume and mass of adsorbent is compared to a control which contains no adsorbent. The adsorbent masses ranged from 0.2 to 60 g. Amount of adsorbent was increased for increasing water content. For each adsorption isotherm, six different adsorbent masses were used with three replicates for each mass. The adsorbent was introduced into glass bottles with a volume of 63 or 248 ml. The bottles were wrapped in paper to prevent photo-decomposition of the VOCs and sealed with teflon Mininert valves (Dynatech, Baton Rouge, LA). A volume of 2.5 ml of air in each bottle was replaced by an equivalent volume of saturated VOC vapor. All bottles were rotated for 24–36 h at 25 °C to reach equilibrium. Preliminary work showed that equilibrium was reached after this period of time. One ml of headspace was removed from each bottle with a gas-tight syringe (Hamilton 1001) and analyzed on a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector. The relative humidity at each water content was determined by measuring it in similarly prepared bottles. Relative humid-ity of the samples was measured with a certified NIST traceable digital hy-grometer (Fisherbrand) with an error of $\pm 1.5\%$ in the 10 to 90% range. Water contents were measured by weighing samples dried in an oven for 24 h at 105 °C. The water contents and the corresponding relative humidities used in the EPICS experiments are summarized in Table 2.

A high vacuum (HV) technique [26] was used to obtain data at the higher relative vapor pressure range than was obtained with the EPICS method up to near saturation. In this technique, an electrobalance located inside a glass vacuum chamber measured the weight change of about 0.5 g of a soil sample upon adsorption. The chamber is evacuated with a mechanical pump and a turbomolecular pump to vacuums as low as $10^{-3}$ Pa. Care was taken so as not to have any static charge interference with the weight measurements. The temperature measured at the vicinity of the soil sample was monitored continu-ously and was within $\pm 0.5$ °C of the experimental temperature of 25 °C. Liquid sources of water, TCE, and toluene connected to the chamber via Kontes high vacuum glass valves were opened to allow evaporation into the chamber. The vapor pressures were determined by a capacitance manometer. The relative vapor pressures were then determined by dividing the measured vapor pres-sures by the published values of the saturated vapor pressure at 25 °C. For binary experiments of water and toluene, water was first allowed to evaporate

TABLE 2

Water content (W) (mg/g, dry weight basis) and corresponding relative humidities (RH) in the soils used in the adsorption experiments

| EPICS[a] | Toluene on sand | | TCE on sand | | Toluene on loam[b] | | TCE on loam | | Toluene and TCE on | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | sand | | loam | |
| | W | RH | W | RH | W | RH | W | RH | W | RH | W | RH |
| | 1 | 0.12 | <1 | 0.07 | 8 | 0.16 | 8 | 0.16 | 2 | 0.13 | 32 | 0.65 |
| | 5 | 0.32 | 5 | 0.25 | 24 | 0.38 | 23 | 0.38 | | | | |
| | 7 | 0.65 | 7 | 0.65 | 31 | 0.65 | 31 | 0.65 | | | | |

| HV[c] | Toluene on sand | |
|---|---|---|
| | W | RH |
| | 1 | 0.10 |
| | 7 | 0.656 |

[a] EPICS = equilibrium partitioning in closed system technique.
[b] Yolo silt loam.
[c] HV = high vacuum technique.

from the liquid reservoir into the chamber. Once equilibrium at the desired relative humidity was reached, toluene was allowed to evaporate in increments until equilibrium was attained. One set of measurements of toluene adsorption at each relative humidity was obtained. The water content and relative humidity data are given in Table 2.

## 4. Results and discussion

### 4.1. Single species systems

Figs. 3 and 4 contain isotherms of TCE and toluene adsorption on the oven-dried Yolo silt loam and sand at 25 °C, respectively. They indicate that the EPICS data connect reasonably well with the HV data for TCE and less so for toluene. The EPICS data are used to investigate the applicability of MBET at low $x_i$ values. The value of $B_i$ and $w_i^m$ for our VOCs and soils were obtained by fitting eq. (2) to the $x_i$ range between 0.05 and 0.3. These values were then used to fit the linearized form of eq. (1) for single species adsorption [27] to the full range of the adsorption data to find the best value of $n$. These data and the $R^2$ values for the fit of eq. (2) are summarized in Table 3. Figs. 3a and 4a show that the MBET equation generally underpredicts adsorption capacity at low $x_i$ values. Even though there was some difficulty in obtaining a good match between the EPICS and the HV data for toluene, the underprediction is most likely the result of the presence of adsorption sites of a higher heat of adsorption than those which are occupied at monomolecular surface coverage [28]. After the most active sites have been covered, the properties of the rest of the
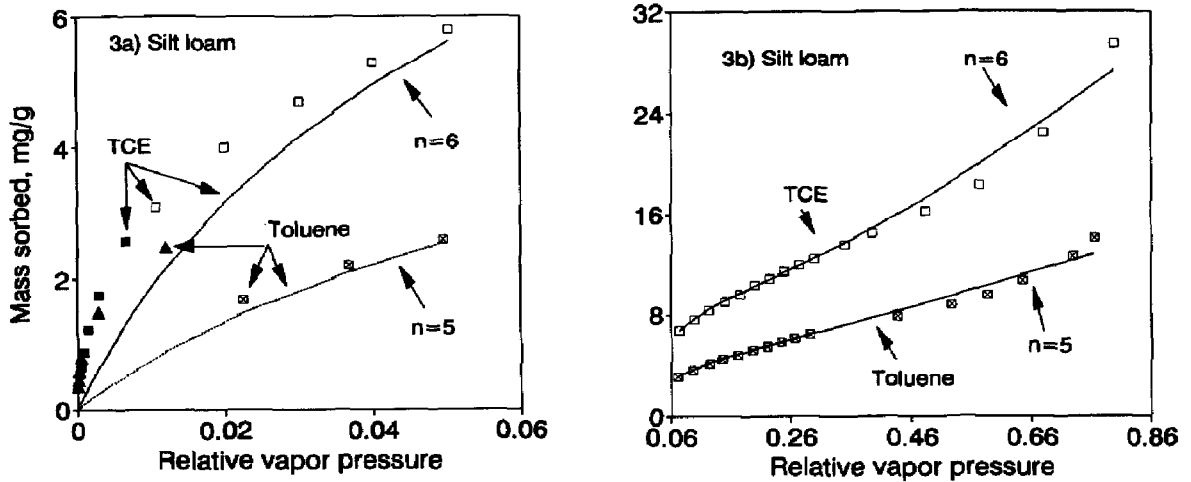
Fig. 3. Adsorption isotherms of TCE and toluene on Yolo silt loam at 25 °C. The values of $n$ given on the figures are the best fit values and the solid lines are the resulting curves. Fig. 3a shows the EPICS method as well as the first few of the HV method data. Fig. 3b includes only the HV data at higher $x$ range.
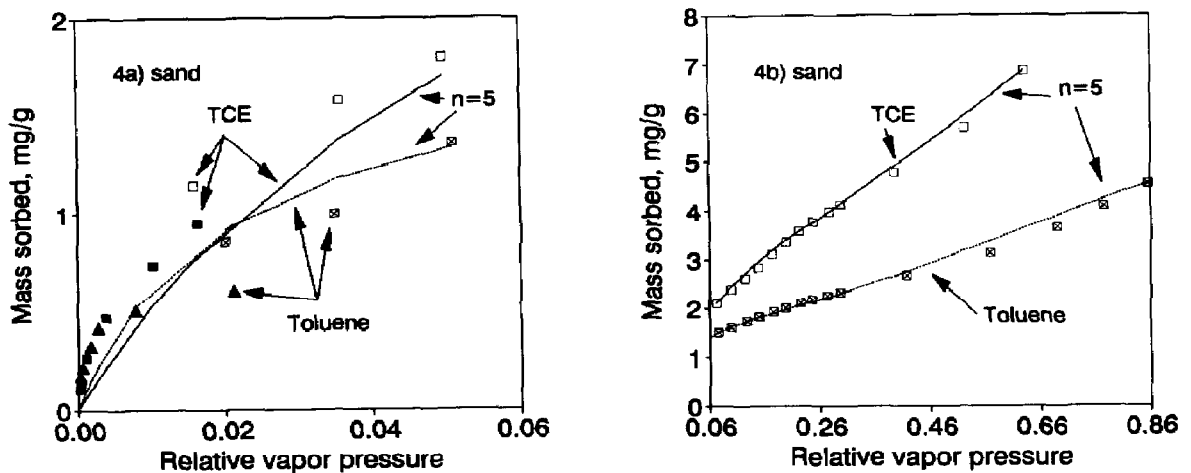


Fig. 4. Adsorption isotherms of TCE and toluene on sand at 25 °C. The values of $n$ given on the figures are the best fit values and the solid lines are the resulting curves. Fig. 4a shows the EPICS method as well as the first few of the HV method data. Fig. 4b includes only the HV data at higher $x$ range.

surface are similar to those of a homogeneous surface for which the MBET is much more suited. We subsequently used the method of Joyner et al. [27] in which the full range of adsorption data (EPICS + HV) is used to fit $B_i$, $w_i^m$, and $n$. However, the resulting values did not model the low $x_i$ range any better (data not shown).

Table 3 indicates that the monolayer capacities, $w_i^m$, are higher on Yolo silt loam than on sand in accordance with the silt loam's higher external surface

TABLE 3

Values of $B_i$, $w_i^m$, and the goodness-of-fit $R^2$ values for the fit of eq. (2) to the appropriate range (relative vapor pressure from 0.05 to 0.3) of the adsorption data for TCE, toluene, and water on dry sand and Yolo silt loam. The value of $n$ was then obtained by fitting the single species form of eq. (1) to the full range of adsorption data with the calculated values of $B_i$ and $w_i^m$

| Compound | Quantitiy | Adsorbent | |
|---|---|---|---|
| | | Sand | Yolo silt loam |
| TCE | $B$ | 18.4 | 23.1 |
| | $w^m$ (mg/g) | 3.3 | 9.7 |
| | $R^2$ | 0.998 | 0.999 |
| | $n$ | 5 | 6 |
| Toluene | $B$ | 55.3 | 16.1 |
| | $w^m$ (mg/g) | 1.7 | 5.3 |
| | $R^2$ | 1.000 | 1.000 |
| | $n$ | 5 | 5 |
| Water | $B$ | 25.7 | 17.6 |
| | $w^m$ (mg/g) | 2.3 | 8.5 |
| | $R^2$ | 0.999 | 0.999 |
| | $n$ | 5 | 7 |

area. The monolayer capacity for water should probably be accepted only as a fitting parameter since water does not coat the surface uniformly [29]. The $B$ values for Yolo silt loam and sand do not correlate well with the trend in polarity. The $B$ values for water are expected to be higher than the VOC species considering energy of adsorption alone. The $B$ values reported by Chiou and Shoup [3] increase as polarity of adsorbates increases. The data of Poe et al. [8] indicate similar behavior for adsorption of nonpolar to more polar compounds on a sandy loam and a silty loam soil. However, the correlation between $B$ and polarity breaks down in their silty clay loam soil. On this soil, the least and the most polar compounds have similar $B$ values which are smaller than the values for compounds of intermediate polarity. The parameter $B$ directly reflects the relative strength of adsorption arising from the different heats of adsorption. Higher strengths of adsorption are signified by higher negative values of $\Delta H_s$. Therefore, the actual value of $B$ is indicative of the degree to which a compound might compete for adsorption sites with other compounds and would be expected to increase with the polarity of adsorbate species. However, the exact relationship between $B$ and $\Delta H_s$ is at best only qualitative [10]. This is since, firstly, the actual amount adsorbed depends on the site distribution of energies for adsorption. The uniform distribution of site energies, as assumed by the BET theory, cannot be assumed for soils due to differences in the chemical nature of the surfaces [30] and the nature of the cations present on different exchange sites [14]. Secondly, porous adsorbents like soils are characterized by a range of pore sizes arising from particle size distribution, structure, and packing [31]. The actual surface area available for
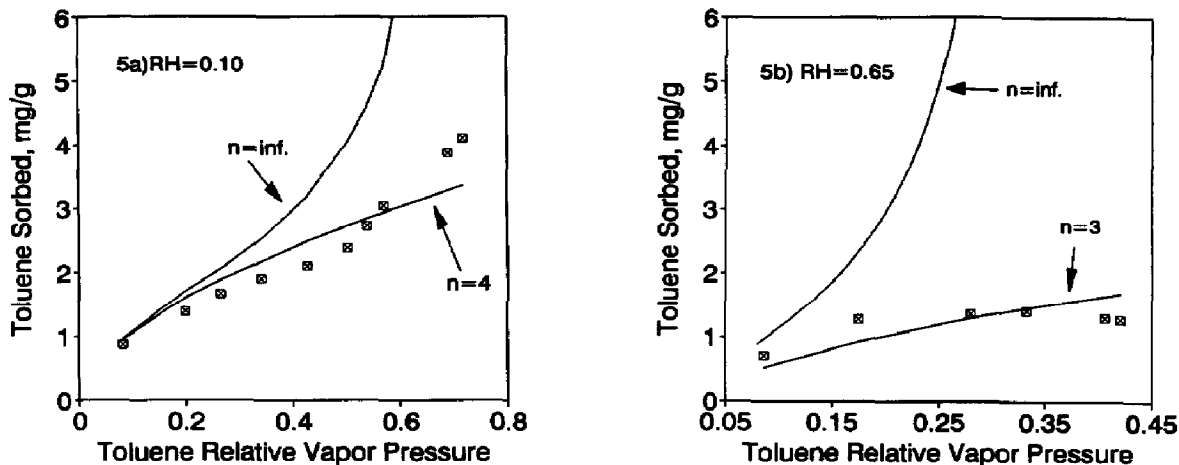
Fig. 5. Toluene vapor adsorption isotherms on sand at two relative humidities. Squares are data measured using the HV apparatus and the lines are from the MBET model with the given best-fit $n$.

adsorption of any given compound depends on whether the adsorbate molecule can reach the adsorbing sites. The larger the adsorbate molecule relative to the pore size, the less adsorption is expected to occur at any given relative vapor pressure.

### 4.2. Binary systems

Fig. 5 contains the fit of the MBET model to toluene adsorption data on sand at two relative humidities. At RH = 0.10 the mass of toluene adsorbed is only slightly less than for adsorption on dry sand (Fig. 4b). At this RH, the amount of water is less than half a monolayer of water coverage on sand (Table 1). According to Quirk [29], water adsorbed at this RH is not thought to cover the soil surfaces uniformly but to congregate around high adsorption sites. Even though the adsorption of toluene on mineral matter is expected to be mostly curtailed by the presence of water molecules [3], higher energy (possibly still bare) sites are apparently still available for toluene adsorption. A similar conclusion was reached by Pennell et al. [14] when looking at *para*-xylene adsorption on Na-saturated kaolin at RHs lower than required to form a monolayer of water coverage. The value of $n = 4$ fitted to the data is one less than $n = 5$ fitted to the dry adsorption data on the same soil. At RH = 0.65 (Fig. 5b), sorbed amount levels out with increasing toluene relative vapor pressure. The last two measurement values are actually slightly less than the previous two possibly from electrical drift of the microbalance [26]. The value of $n$ used to fit the data is reduced to three in accordance with lower adsorption amounts at the higher water contents.

Figs. 6a–d contain the fit of the MBET model to adsorption data of toluene and TCE at low $x_i$ range on sand and Yolo silt loam at several RH values. The lowest RH values in each graph correspond to less than one molecular layer of
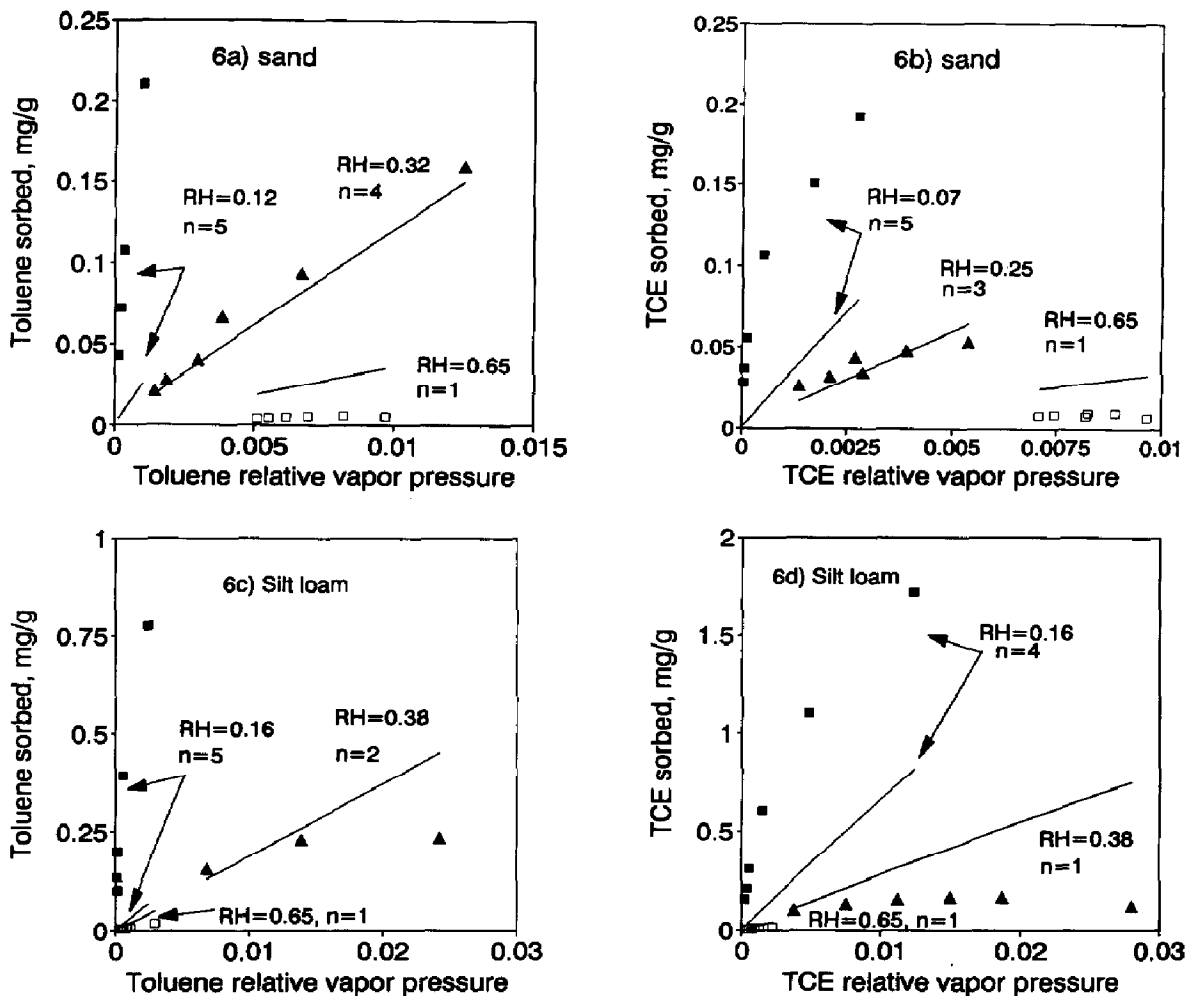
Fig. 6. Binary vapor adsorption of TCE or toluene at several RHs on sand and Yolo silt loam. The solid lines are the MBET predictions with the corresponding RH and the best-fit value of $n$. (a) Toluene on sand, (b) TCE on sand, (c) toluene on silt loam, and (d) TCE on silt loam.

water coverage on the adsorbent surface. At the lowest RHs, the MBET underpredicts the sorbed mass for values of $n$ ranging from 2 to the value fitted to dry adsorption data. This behavior is similar to the underprediction of adsorption on dry adsorbents in the low vapor pressure range. The explanation of this behavior is similar to the one given for the single-species cases and indicates that water does not coat the soil surfaces uniformly as Quirk [29] has discussed. No such behavior was seen at the higher toluene vapor pressures (Fig. 5a) most likely because a monolayer of water and toluene was already formed on the sand surface. Further adsorption, therefore, took place on a more energetically uniform surface.

The intermediate RH values correspond to water contents between one and two molecular layers of coverage. The fit of the MBET model is much better

than for the low RH cases. Most, if not all, of the energetic heterogeneity on sand surfaces has been eliminated by water coverage [28], resulting in a more homogeneous surface for further adsorption. The MBET fit is less satisfactory on the more heterogeneous silt loam than the sand. Notice that the fitted values of $n$ are becoming smaller as RH increases and are associated with lower adsorption amounts of TCE and toluene.

At RH = 0.65, or about two molecular layers of water coverage, the measured isotherms show reduced adsorption capacity. The MBET overpredicts adsorption for both VOCs on both soils even at the lowest possible $n$ value. The MBET assumes ideal mixed liquid adsorbate corresponding to complete miscibility of adsorbed species. As the number of water layers on the adsorption surface increases, the dissolution in water is thought to dominate the uptake process of VOCs on saturated soils [5]. The adsorption process of water and VOCs on mineral matter changes to a dissolution process of VOCs in water. It is, however, doubtful that the MBET equation leads to an adequate vapor–liquid solution theory at this and higher RH values [13].

The final binary system studied is that of *para*-xylene and water adsorption on Na-saturated kaolin performed by Rhue et al. [9]. Their measured adsorption values, the MBET model predictions, and the predictions using eq. (3) which was derived from the basic equations given in the Rhue et al. (1989) paper are included in Table 4. The $B$ and $w_i^m$ values used in the MBET model were obtained by fitting eq. (2) to appropriate range ($x$ from 0.05 to 0.3) of the single-species data given in their paper. The lowest and the highest *para*-xylene relative vapor pressures are within the range of HV data used in our experiments with TCE and toluene. At low to intermediate RH values, the fit of the MBET equation to the *para*-xylene adsorption data is much better than the fit of eq. (3). The predictions of eq. (3) become comparable to MBET only at high RH values when both predict the sorbed mass of *para*-xylene well. At lower RHs, the MBET slightly underpredicts the measured sorbed amount. However, at RHs close to 0.65, the measured sorptions are predicted well. The *para*-xylene solubility in water is 198 mg/l (25 °C) compared with 1100 mg/l for TCE (25 °C) and 515 mg/l for toluene (20 °C) [32]. Even though solubility values alone cannot be used to partition adsorption between water and mineral phases at these water contents [5], we would still expect the ideal solution assumption in MBET to be more restrictive for less soluble *para*-xylene than the more soluble toluene and TCE. The relatively good prediction of *para*-xylene adsorption at these higher water contents is perhaps indicative of the fact that the ideality of the adsorbed mixture is not a very restrictive assumption in developing the MBET model at these water contents. The MBET model shows much improvement over eq. (3) in predicting adsorbed amounts of *para*-xylene over a relatively wide range of water and *para*-xylene vapor pressures.

## 4.3. Ternary systems

Data were obtained on adsorption of TCE and toluene from mixtures with water on our adsorbents using the EPICS method. The comparisons between

TABLE 4

Comparison of MBET model predictions with predictions from eq. (3) and with the measured values of adsorption of *para*-xylene and water vapors on Na-saturated kaolin reported in Rhue et al. [9]

| Water relative vapor pressure | *para*-Xylene relative vapor pressure | *para*-Xylene mass sorbed (mg/g) | Simulated sorbed mass (mg/g) | | Best fit $n$ |
|---|---|---|---|---|---|
| | | | Eq. (3) | MBET | |
| 0.084 | 0.390 | 7.11 | 31.15 | 5.90 | 6 |
| 0.095 | 0.379 | 6.56 | 29.55 | 5.54 | 5 |
| 0.100 | 0.132 | 3.96 | 10.18 | 2.45 | 5 |
| 0.190 | 0.086 | 2.61 | 5.37 | 1.40 | 4 |
| 0.22 | 0.18 | 3.87 | 10.43 | 2.63 | 5 |
| 0.228 | 0.424 | 7.04 | 24.06 | 5.70 | 5 |
| 0.239 | 0.281 | 5.23 | 15.49 | 3.89 | 5 |
| 0.262 | 0.171 | 3.5 | 8.87 | 2.43 | 5 |
| 0.39 | 0.156 | 2.34 | 5.53 | 2.08 | 3 |
| 0.517 | 0.187 | 1.85 | 4.15 | 1.75 | 2 |
| 0.658 | 0.069 | 0.45 | 0.77 | 0.34 | 4 |
| 0.67 | 0.286 | 2.77 | 2.97 | 2.87 | 3 |
| 0.676 | 0.164 | 1.41 | 1.64 | 1.38 | 3 |

TABLE 5

Comparison of measured and calculated adsorption of TCE and toluene from their ternary mixture with water on the adsorbents. The $n$ values given are the best fit values. Measured RHs are 0.10 for sand and 0.65 for loam

| TCE relative vapor pressure | Toluene relative vapor pressure | Mass TCE sorbed (mg/g) | Mass toluene sorbed (mg/g) | Simulated sorbed mass (mg/g) | |
|---|---|---|---|---|---|
| | | | | TCE | Toluene |
| *Sand* | | | | $n=4$ | $n=4$ |
| 0.034 | 0.036 | 0.543 | 0.530 | 0.428 | 0.571 |
| 0.014 | 0.004 | 0.516 | 0.244 | 0.231 | 0.084 |
| 0.012 | 0.003 | 0.419 | 0.184 | 0.198 | 0.066 |
| 0.008 | 0.002 | 0.386 | 0.152 | 0.142 | 0.041 |
| *Silt loam* | | | | $n=1$ | $n=1$ |
| 0.0021 | 0.0016 | 0.0126 | 0.0080 | 0.0379 | 0.0109 |
| 0.0012 | 0.0007 | 0.0084 | 0.0038 | 0.0218 | 0.0048 |
| 0.0010 | 0.0006 | 0.0071 | 0.0030 | 0.0176 | 0.0038 |
| 0.0008 | 0.0005 | 0.0061 | 0.0024 | 0.0147 | 0.0031 |
| 0.0005 | 0.0003 | 0.0049 | 0.0018 | 0.0096 | 0.0022 |
| 0.0005 | 0.0003 | 0.0044 | 0.0016 | 0.0082 | 0.0019 |

measured values and values from the MBET model are summarized in Table 5 for sand at RH = 0.10 and Yolo silt loam at RH = 0.65, respectively. With two or more VOCs adsorbing, the adsorption sites not occupied by water molecules are divided between the VOC species based on their strength of adsorption. The higher value of parameter $B$ for toluene compared with TCE on sand indicates higher preference of this soil for toluene than TCE. Not much difference was, however, observed between the adsorption strengths of either TCE or toluene compared with their binary adsorption experiments. At these low concentrations, the major competition for each VOC species seems to be with water and not with each other. At the low RH on sand, the MBET simulates lower adsorbed amounts than what is measured. This is similar to what occurred in the single and binary experiments. At the higher RH on Yolo silt loam, the MBET overpredicts the measured amounts for both VOCs at this RH as similarly occurred in the binary cases. At low VOC relative vapor pressures at these two RHs, their behavior is mainly determined by the presence of water and not the other species.

## 4.4. Significance of n

The fitting of $n$ in addition to $B$ and $w^m$ enables the single-species isotherms to be well characterized over a good portion of their vapor pressure range. The physical meaning of this parameter in such systems is straightforward and is the maximum number of adsorbed layers which can be formed on the adsorbent surface [6]. By analogy, this parameter is the number of layers of mixed adsorbate layers in a multicomponent case [11]. In binary formulations used to date [4, 13], there was no need to define $n$, since $n = \infty$ was used. This is because the amount adsorbed is independent of $n$ at low relative vapor pressures as shown in Fig. 1. The same behavior is observed in Fig. 5 for binary systems of toluene adsorption on wet sand. It is only at the relatively higher $x_i$ range that the $n = \infty$ formulation diverges from a finite $n$ formula. The extent of divergence increases as $x_i$ increases and leads to serious overpredictions of adsorption amounts. Many contaminations of soil and groundwater involve low concentrations of the VOC species. Therefore, setting $n = \infty$ in eq. (1) is a good approximation at low $x_i$ (Fig. 1). However, in cases where higher concentrations are involved, as with concentrations existing close to immobile residual liquid VOCs or around high liquid concentrations from accidental spills or deliberate dumpings, an $n = \infty$ would lead to overestimation of adsorption.

Two hypotheses were proposed earlier to elucidate the correct physical significance of the parameter $n$. The first one is that $n$ is the maximum number of mixed adsorbate layers on the adsorbent surface as in Hill's original paper. In this case, when one species has a much higher relative vapor pressure compared with other species, the value of $n$ in the isotherm for all species is expected to approach the $n$ for the one species with high relative vapor pressure. However, in our simulations the value of $n$ for all VOC adsorbents decrease as RH increases rather than approaching the $n$ values fitted to water adsorption data. We therefore investigate our second hypothesis in which $n$ is

an 'equivalent' maximum number of layers. It applies to adsorption of VOCs onto a soil–water complex and is a function of RH (or water content). In this soil–water system, VOC molecules can penetrate the surface (e.g., dissolve in water) as well as adsorb onto mineral surfaces directly. The minimum value of $n$ ($n_{min}$) is equal to the total amount adsorbed $w_i$ spread over the adsorbent external surface area $S_{ext}$. It is given by

$$n_{min} = \frac{w_i A_i N}{M_i S_{ext}} \tag{4}$$

where $w_i$ is a measured mass of adsorbate per mass of adsorbent (g/g), $A_i$ is the projected area of one molecule (m²/molecule), $N$ is the Avogadro number ($= 6.022 \times 10^{23}$ molecules/mol), and $M_i$ is the molecular weight for species $i$ (g/mol). The parameter $A_i = 1.091(M_i/d_i N)^{2/3}$ [33], where $d_i$ is the liquid density of the species. Eq. (4) indicates that $n_{min}$ increases as $w_i$ increases. Note that the value obtained from eq. (4) is not an integer. The value of $n$ chosen for fit to eq. (1) must at least be the integer higher than $n_{min}$ determined from an experiment which involves the highest VOC concentration deemed probable for the case being modeled. The value of $n$ ranges from this minimum value to the maximum used to fit the dry adsorption isotherm. For example, for toluene adsorption data on sand (Fig. 5), the highest measured $w_i$ at an RH of 0.18 and 0.65 give $n_{min} = 2.3$ and $n_{min} = 0.73$, respectively. The fitted values of $n$ are 4 and 3, respectively. Both of the fitted $n$ values are higher than $n_{min}$ and lower than the $n$ fitted to dry adsorption data ($n = 5$, cf. Table 1). Similar results were observed for Rhue et al. [9] data. For ternary and larger multinary cases, the value of $n$ for less highly adsorbed species would not only depend on RH but also on the vapor pressures of the other more highly adsorbed species. Based on these data alone, the second hypothesis cannot be exclusively accepted or rejected. However, the decrease of the value of $n$ is over a relatively small range which would make its use as a fitting parameter relatively convenient in modeling multi-component adsorption.

## 5. Conclusions

The extension of the general BET adsorption equation to multicomponent adsorption as proposed by Hill [11, 12] was tested on binary and ternary systems of TCE, toluene, and water vapors on a sand and Yolo silt loam soil. The model inputs are the monolayer adsorption capacity ($w_i^m$), a constant related to heats of adsorption ($B_i$), and a constant signifying the number of adsorbed layers on the adsorbent surface ($n$). The first two constants were obtained by application of the model to single-species adsorption isotherms. The last constant ranges from a minimum integer value larger than the total amount adsorbed spread over the soil external surface area to a maximum value obtained from the single species adsorption isotherm.

This model was reasonably successful in describing adsorption of toluene from its binary vapor mixture with water on the sand over toluene vapor pressures range above about 0.1 and at two relative humidities (RH) corresponding to less than one and about two molecular layers of water. At lower TCE and toluene relative vapor pressures, the model was applied to their adsorption on the sand and Yolo silt loam at three RH values. At RH values corresponding to less than a monolayer of water coverage, it underpredicted adsorbed amounts. At intermediate RH values corresponding to between approximately one and two molecular layers of water coverage, predictions were successful. At the highest RH value of 0.65, corresponding to about two molecular layers of water, the MBET equation overpredicted the adsorbed amounts. The MBET equation was more successful than a method based on the equations of Rhue et al. [9] in describing adsorption of para-xylene from its binary mixture with water over a wide range of para-xylene and water relative vapor pressures. Adsorption experiments in the ternary systems of TCE, toluene, and water did not indicate any major decrease in adsorption of any of the VOCs as a result of the presence of the other compounds at the RHs studied.

The maximum number of adsorption layers is an important parameter in correctly modeling multicomponent adsorption. Even though its physical significance is still somewhat ambiguous, its value was confined to a narrow range for the VOCs and soils tested in this study. For simulations at low VOC relative vapor pressures, the amount adsorbed is irrespective of the value of $n$ and a simplified equation based on $n = \infty$ can be used. At higher relative vapor pressures, the choice of $n = \infty$ leads to overestimation of adsorption and a finite $n$ should be used.

The MBET equation can successfully be used to model VOC adsorption on geological material and soil over the range of water content corresponding to between one and two molecular layers. It underpredicts the adsorption amount at lower water contents and low VOC relative vapor pressures. At higher water contents it lacks a suitable vapor solution theory so that the measured adsorption isotherms have to be employed. However, the amount of overprediction may be small enough to render its use for modeling purposes worthwhile.

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