



Adsorption of chlorinated hydrocarbon vapors onto soil in the presence of water

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Received 20 July 2000; received in revised form 9 February 2001; accepted 9 February 2001

Abstract

Chlorinated solvents partition readily into the vapor-phase in unsaturated soils. Sorption from the vapor-phase affects both transport and recovery. The Brunauer–Emmett–Teller (BET) isotherm has been used to model adsorption of chlorinated solvent vapors; however, the BET equation is not accurate above reduced vapor pressures (p/p_{sat}) of 0.35. New measurements of chlorinated alkane sorption have been used with a modified BET equation (MBET) to model the adsorption isotherms for five solvents. The MBET equation was found to fit experimental data accurately, especially at high reduced vapor pressures. The capacity of sandy loam soil to adsorb organic vapors decreased with increasing water content, probably due to less soil surface available for sorption. This effect is most evident at reduced vapor pressures greater than 0.5. Adsorption is related to distribution of excess surface energy, the number of molecular layers of water sorbed at the surface, and solute polarity. Results suggest that water films contain areas of high interfacial energy that interact with solute molecules via induced electrostatic forces. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Adsorption; Chlorinated solvents; Soil; Soil moisture

1. Introduction

Distribution of organic contaminants among all phases in a soil system must be quantified to simulate transport and to design effective remediation processes. Partitioning of solutes in water-saturated soils has been investigated for many common organic contaminants on soils with diverse properties [1–5]. Investigations concerned with sorption processes in

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unsaturated soils suggest that sorption of vapor-phase contaminants in water-unsaturated soils contributes to retardation of diffusive transport [6–8].

Several soil properties influence the amounts and energies of adsorption in unsaturated systems. For oven-dried soils, adsorption correlates directly to total surface area [9–11]. The importance of adsorbent properties, such as organic matter content and excess surface energy, increases with soil water content as less polar organic molecules compete for available sorption sites [12,13]. Similarly, sorbate properties affect sorption most when soil water is present at levels below saturation. The presence of a preferential wetting fluid, i.e. liquid or vapor water, has a major effect on sorption of non-electrolyte organic vapors on soil. Investigators have suggested that sorption of organic vapors on porous sorbents decreases with increasing soil moisture content [10–12,14–16].

Isotherms for organic vapor adsorption onto soils at low reduced vapor pressures, i.e. p/p_{sat} (partial pressure normalized to vapor pressure, are consistent with Brunauer–Emmett–Teller (BET) classifications. Type II isotherms are observed at low soil water content, indicating progression from monolayer adsorption to multi-layer adsorption to capillary condensation. Above 50% relative humidity, adsorption isotherms for several chlorobenzenes on soil are linear [14]. BET parameters have been determined for many sorbent/sorbate systems [11,14]. The BET equation can be used to estimate available surface area and interaction energies; however, this use is valid only for low sorbent concentrations, i.e. $0.05 < p/p_{\text{sat}} < 0.30$. Ricca and Bellardo [17] found that estimates of monolayer coverage varied as much as 35% for a given isotherm, depending on the range of relative vapor pressures used in the analysis. Models utilizing data for higher relative vapor pressures yielded higher values for monolayer coverage. Jurinak and Volman [18] measured ethylene dibromide adsorption onto soil; the BET equation fit data well, at reduced vapor pressures up to 0.5, but overestimated adsorption at higher reduced vapor pressures.

Predictive failures of the BET equation at high relative vapor pressures is a consequence of the assumptions of the model. The unmodified BET equation assumes an infinite number of monolayers can form on a sorbent surface. In porous media, such as soil, adsorption is limited by pore size distribution. As adsorbent molecules accumulate in multiple layers, total adsorption is constrained by the dimensions of intra- and inter-particle pores. The effects of pore size distribution become evident at high reduced vapor pressures, i.e. $p/p_{\text{sat}} > 0.5$, well below water-saturation. Organic species trapped as non-aqueous phases in the unsaturated zone express vapor pressures approximately equal to saturation; the BET equation cannot predict adsorptive behavior in such systems.

Experiments were performed to evaluate the effects of moisture and adsorbate properties on adsorption of chlorinated organic compounds from the vapor-phase onto a low-carbon soil. Data were used to test a model suited to high reduced vapor pressures. Adsorption of 1,2-dichloroethane (DCA), 1,1,1-trichloroethane (TCA), chloroform (TCM), trichloroethylene (TCE) and carbon tetrachloride (CT) onto a sandy loam (Adelphia soil), at soil water contents of 0 wt.% (oven-dried) to 46.1 wt.% (field capacity), was measured.

2. Materials and methods

Adsorption of the five chlorinated hydrocarbons (CHs) studied by Lam [10], from the vapor-phase onto a sandy loam, was measured at several soil water contents by equilibrium

Table 1
Properties of Adelphia soil

Constituent	Dry weight (%)
Physical composition	
Sand	71.0
Silt	13.8
Clay	13.8
Organic matter	1.4
USDA texture classification	Sandy loam
Other properties	
Surface area (BET)	15.1 (m ² /kg)
Cation exchange capacity	7.1 (meq/g)
pH	5.2

headspace analyses. The measurement technique was derived from methods used previously by Lam [10] and Loehr and English [19], with two major modifications. Sandy loam soil was obtained from the Rutgers University experimental farm at Adelphia (NJ); properties are summarized in Table 1. Soil was sterilized by γ -radiation rather than autoclaving because the latter has been shown to change soil pore structure [20]. Glassware was treated with 30% nitric acid to minimize adsorption of CHs onto surfaces of experimental systems. CH choice was based on diversity of dipole moments and solubilities, as well as frequency of occurrence at sites contaminated with chlorinated hydrocarbons.

Oven-dried soil was prepared by drying at 105°C for 24 h. Lam [10] concluded that soil dried in this manner retains surface hydration but has bulk water removed. Moist soil was prepared by adding 0.005 M calcium chloride solution to air-dried soil. The latter contained 1–3 g of water/100 g of dry soil, depending on the relative humidity of the laboratory. Air-dried and moistened soils were homogenized on a rotating mixer for 24–72 h. Soil samples were packaged in 500 ml EPA amber bottles, in amounts of 300 g, and γ -irradiated at the Virginia Nuclear Reactor Facility (Blacksburg, VA).

Exposure to extraneous contamination was minimized by moisture addition and homogenization prior to irradiation. Moisture content was verified by over-drying irradiated soil samples taken at the time of experiments.

In an individual adsorption experiment, 3–4 g of irradiated soil was placed into a 40 ml volatile organic analysis (VOA) vial. Vials were closed with Mininert TeflonTM valves (see Fig. 1). Valve caps held PTFE-lined septa to facilitate liquid injection and headspace sample extraction. Septa were replaced between experiments.

Predetermined volumes of liquid solvents were injected into small glass tubes in the VOA vials via a gas-tight syringe. Tubes were 8 mm o.d. standard-bore process pipe cut into 5 cm lengths. One end of each tube was sealed with Pyrex glass; the edges of open ends were fired to prevent splintering. After solvent injection, vials were held at 21°C for at least 24 h, Lam [10] found that equilibrium is reached in less than 24 h.

After equilibration, a headspace sample was taken with a “Pressure-Lok” gas-tight syringe and injected into a Hewlett-Packard 5890 gas chromatograph equipped with an HP 5970B mass selective detector. Sample volumes were varied, based on anticipated vapor-phase

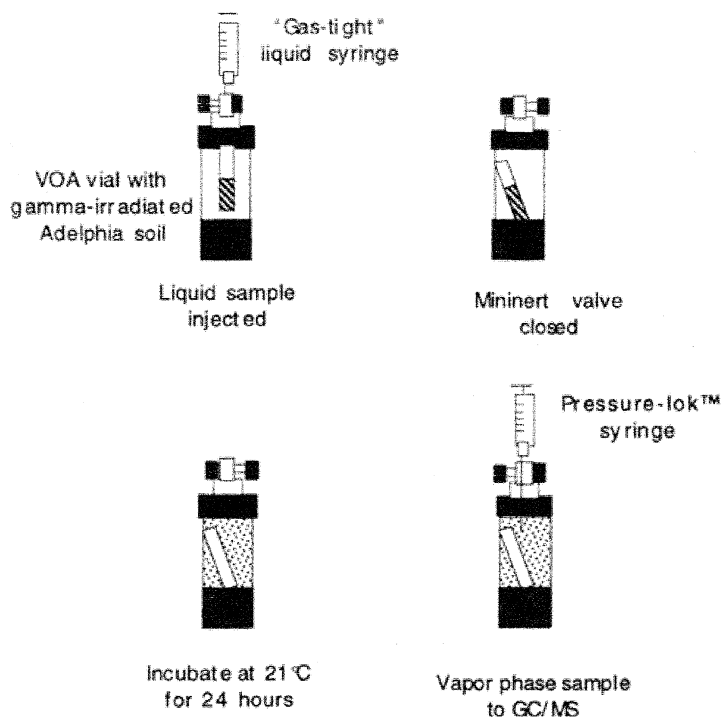


Fig. 1. Apparatus and method for determining vapor-phase adsorption of chlorinated hydrocarbons onto soil.

composition, to maintain concentrations within the detection limits of the analytical equipment. Control experiments were run with known volumes of liquid solvent and no soil. Repetitions varied by no more than 5%, on a molar basis; data from experiments with controls falling outside 5% limits were rejected. VOA vials and glass tubes were cleaned between experiments by washing with Sparkleen™, rinsing twice with DI water and immersion in 30% nitric acid for 24 h. After acid-washing, glassware was rinsed seven times with distilled water and dried at 105°C for 24 h.

Relative humidity as a function of water content of Adelphia soil was measured in a similar manner. VOA vials were packed with up to 25 g of soil of known moisture content, capped and equilibrated for 24 h. After equilibration, the vapor-phase was sampled with a "Pressure-Lok" syringe and analyzed by gas chromatograph. Soil was dried at 105°C for 24 h and weighed to determine final moisture content. Comparisons of initial and final weights indicated that losses from the vials were negligible.

3. Results and discussion

Adsorption of five one- and two-carbon chlorinated hydrocarbons onto a sandy loam was measured at 21°C and several soil water contents. Water contents varied from 0%

(oven-dried) to 46% (field capacity), on a dry weight basis. Adsorption capacity and heat of adsorption varied with soil water content as well as sorbate polarity. Several adsorption isotherm models were tested. Of the models considered, only a MBET model yielded consistent estimates of adsorptive capacity over a wide range of vapor pressures.

Area available for adsorption in porous media is at surfaces of intra- and inter-particle pores. The BET model only predicts adsorption accurately at low reduced vapor pressures, i.e. the BET model yields good estimates for $0.005 < p/p_{\text{sat}} < 0.30$, where separate organic phases are not present as capillary condensate or trapped bodies at inter-particle contact points. Drain and Morrison [21] developed the MBET model to fit type II isotherms at high relative vapor pressures. By assuming multi-layer formation is limited by competition between surfaces of intra- and inter-particle pores, the MBET adsorption isotherm is written as

$$C = \frac{\{(\Theta)(A)\}}{\{1 + (K - 1)(p/p_{\text{sat}}) - K(p/p_{\text{sat}})^{n+1}\}} \quad (1)$$

where

$$\Theta = \left\{ \frac{[C_A K (p/p_{\text{sat}})]}{[1 - (p/p_{\text{sat}})]} \right\}$$

$$A = \left\{ 1 - (n - 1) \left(\frac{p}{p_{\text{sat}}} \right)^n + n \left(\frac{p}{p_{\text{sat}}} \right)^{n+1} \right\}$$

and n is average number of layers; it is an average over the entire adsorbent surface and will be overpredicted for inter-particle surfaces because of capillary condensation in intra-particle pores. C is the adsorbed solute concentration (mmol/kg) at a specified reduced vapor pressure (p/p_{sat}) and C_A the monolayer adsorption capacity. K is related to the heats of adsorption (Q_s) and condensation (Q_c) for adsorbed species, as follows

$$K = a \left[\left\{ \exp \left(\frac{Q_s - Q_c}{RT} \right) \right\} \right] \quad (2)$$

where a is a dimensionless constant. The value of K characterizes the shape of MBET isotherms. For $K > 40$, the inflection point for the transition from monolayer to multi-layer coverage is distinct. For $K < 20$, the transition is gradual, indicating the energy of interaction at less than monolayer coverage is comparable to the heat of condensation of adsorbate. The MBET model has been used to obtain adsorption isotherms, at reduced vapor pressures greater than 0.5, for toluene and trichloroethylene on porous adsorbents [22].

Langmuir, BET and MBET models are compared against experimental data for TCM on oven-dried soil in Fig. 2. For monolayer adsorption ($p/p_{\text{sat}} < 0.2$), the three models fit the data well. At reduced vapor pressures of 0.5 and higher, the BET model significantly overestimates adsorption and the Langmuir model is inadequate. The MBET model fits the experimental data for TCM on oven-dried soil; the regression optimizes at an n of 7.6. The MBET model is very sensitive to n above the inflection point that accompanies the transition from monolayer to multi-layer coverage (see Fig. 2).

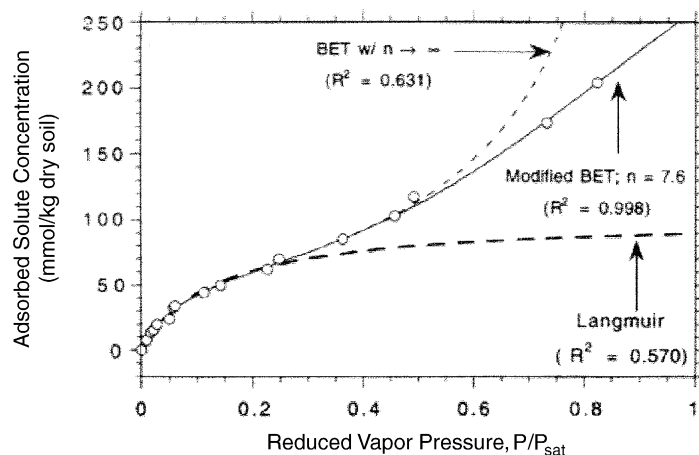


Fig. 2. Comparison of adsorption isotherm models with experimental data for TCM on oven-dried soil.

3.1. Influence of soil water content on adsorption

Adsorption data for 1,2-DCA, 1,1,1-TCA, TCM, TCE and CT onto sandy loam was fit to the MBET model. Monolayer adsorption capacities, K_s for the MBET model and estimates of multi-layer formation are summarized in Table 2. Correlation coefficients were greater than 0.982, in all cases; these correlations are better than fits to the BET model reported by Lam [10]. At water contents greater than 0 wt.%, dissolution into bound water and adsorption at the gas water interface compete with direct adsorption of solvent on soil. In all cases, dissolution of adsorbed solvent into soil organic matter contributes to overall uptake, also.

The total surface area of oven-dried soil, as measured by N_2 -BET analysis, is approximately $15 \text{ m}^2/\text{kg}$. Except for 1,1,1-TCA, monolayer adsorption capacities suggest areas about 80% of this value. The large diameter of the 1,1,1-TCA molecule, i.e. 18% greater than 1,2-DCA, may account for the difference. Transition from mono- to multi-layer adsorption occurs between $0.2 < p/p_{\text{sat}} < 0.4$; capillary condensation is predicted to occur at $p/p_{\text{sat}} > 0.4$ by the Kelvin equation.

In all cases, monolayer adsorption capacity and K decrease with increasing soil moisture content. Large decreases are associated with the process by which soil is dried, i.e. the dominant adsorption mechanism differs for oven-dried and air-dried soils. After oven-drying, solvent vapor adsorbs directly onto hydrated mineral sites and partitions into organic matter.

Adelphia soil has 1.4% organic matter (on a dry weight basis); in the absence of water, adsorption is a function of available mineral surface area. As soil water content increases, fewer mineral sites are available and, at some point, surfaces are covered with sufficient water to negate direct surface interactions.

The heat of adsorption for water vapor onto soil minerals is much greater than the heat of condensation, as indicated by the minimal contact angle between liquid water and dry soils [22]. Water molecules will form a monolayer, hydrating the entire available surface,

Table 2
MBET adsorption model parameters^a

Approximate (g water/100 g soil)	Monolayer coverage (mmol/kg soil)	Monolayer coverage (m ² /kg soil)	Fraction of total surface occupied	<i>K</i>	<i>n</i>
1,2-Dichloroethane					
0.0	63.0	11.85	0.78	6.3	8.0
4.3	32.6	6.13	0.41	4.8	19.7
11.0	12.7	2.39	0.16	2.1	10.9
21.5	10.7	2.02	0.13	1.4	5.4
46.1	9.9	1.85	0.12	0.4	14.4
1,1,1-Trichloroethane					
0.0	44.4	9.83	0.65	15.4	14.9
4.3	20.0	4.42	0.29	3.0	7.9
11.0	11.9	2.63	0.17	1.6	8.3
21.5	8.9	1.97	0.13	1.6	3.2
39.8	2.4	0.54	0.04	1.0	14.1
Trichloromethane (chloroform)					
0.0	61.0	11.59	0.77	14.8	7.6
4.3	27.1	5.15	0.34	3.0	6.1
11.0	13.8	2.63	0.17	2.5	12.4
21.5	6.6	1.25	0.08	2.9	4.7
39.8	3.1	0.59	0.04	2.3	7.7
Trichloroethylene					
0.0	60.4	12.3	0.81	14.0	11.1
4.3	13.8	2.8	0.19	3.1	13.9
10.0	9.2	1.9	0.12	2.4	10.6
21.5	7.4	1.5	0.10	2.2	8.7
46.1	1.6	0.3	0.02	1.4	7.4
Carbon tetrachloride					
0.0	56.1	12.1	0.80	14.3	12.1
4.3	7.3	1.6	0.10	7.3	14.4
8.8	7.0	1.6	0.10	4.1	16.1
21.5	2.5	0.5	0.04	1.6	4.9
46.1	1.4	0.3	0.02	0.9	4.0

^a Five chlorinated solvents on sandy loam at 21°C.

before aggregating in multiple layers. However, surface energies vary greatly and water in multi-layer structures can aggregate at high energy sites. These sites are filled readily, at increased soil water content; soil moisture content increases primarily by pore condensation. Capillary condensation restricts solvent vapor access to interior surfaces for adsorption [11].

Soil moisture is related to gas phase relative humidity [10,14]. The relation is linear to about 90% relative humidity; the slope is a function of soil characteristics, i.e. surface area, surface energy distribution, organic matter content and pore-size distribution. For Quakertown soil, the proportionality factor is 25.1 [10]. In the present study, the correct factor for the relationship between Adelphia soil moisture content and relative humidity

was observed to be 19.4. Soil water contents exceeding 5.15 g of water/100 g of dry soil correlate with 100% relative humidity. At higher soil moisture contents, water accumulates via capillary condensation until saturation occurs.

3.2. Estimates of adsorbate coverage

Based on the assumption that molecular layers are adsorbed evenly, the theoretical number of monolayers can be calculated as a function of soil moisture content. Further assuming that adsorbed vapor density is equivalent to density in the normal liquid state, specific molecular volume (V) is given by

$$V = \frac{MW}{\rho N_0} \quad (3)$$

where MW is molecular weight, ρ the normal liquid density of the sorbate (gm/cm^3), and N_0 Avogadro's number (6.02217×10^{23}). If a spherical configuration is assumed, relative molecular radius (r_{rel}) and area (A_{rel}) can be calculated

$$r_{\text{rel}} = \left\{ \frac{3V}{4\pi} \right\}^{1/3} \quad (4)$$

and

$$A_{\text{rel}} = \pi \left\{ \frac{3V}{4\pi} \right\}^{2/3} \quad (5)$$

The nominal number of adsorbate monolayers can be determined with Eq. (5). Relative saturation is volume of water per unit volume of void space; it is reported as a percent in Table 3. Soil moisture is mass of water per unit mass of dry soil; it is reported as a percent in Table 3. Coverage is area (square meters) of adsorbed water/g of dry soil.

Water molecules aggregate at surface defects and occlusions with high excess energy both before and after monolayer formation. Water molecules adsorb preferentially to minimize

Table 3
Soil water content and layer formation on sandy loam at 21°C

Relative humidity (%)	Relative sat. (%)	Soil moisture content (%)	Coverage (m^2/g)	Layers
0	0.0	0.0	0.0	0.0
7	1.5	0.4	15.2	1.0
21	4.3	1.1	42.5	2.8
46	8.8	2.0	79.5	5.3
53	10.1	2.3	91.2	6.0
58	11.0	2.6	99.3	6.6
86	21.5	5.0	194.8	12.9
98	39.8	9.3	360.7	23.9
100	46.1	10.7	417.6	27.6
100	75.5	17.6	684.1	45.3
100	100.0	23.3	905.9	60.0

surface free energy. At low water contents, insufficient water may be available to form a complete film that is thick enough to overcome localized surface free energy variations of the solid adsorbent. In this instance, the adsorbed liquid film at the interface may contain molecules of greater dipole moment than found at bulk water surfaces. Chlorinated solvents can exhibit interaction energies above those predicted from heats of condensation. Energies of interaction calculated from K in the MBET model are summarized in Table 4. Energies of interaction are less variable at high moisture content and the properties of adsorbed water approximate those of bulk water. Heats of adsorption approach heats of condensation under these conditions. Peterson et al. [23] report similar results for a number of solid sorbents. The properties of bulk water appear to become applicable at approximately four molecular layers of water.

Table 4
Energies of interaction for chlorinated solvents on sandy loam at 21°C

Approximate: g of water/ 100 g dry soil	Q_s (kJ/mol)	Q_s/Q_c
1,2-Dichloroethane		
0.0	39.6	1.13
4.3	39.0	1.11
11.0	37.0	1.05
21.5	35.9	1.02
46.1	33.0	0.94
Trichloromethane		
0.0	40.0	1.20
4.3	36.0	1.08
11.0	35.6	1.07
21.5	36.0	1.08
39.8	35.3	1.06
Carbon tetrachloride		
0.0	38.9	1.20
4.3	37.3	1.15
8.8	35.9	1.11
21.5	33.6	1.04
46.1	32.2	0.99
1,1,1-Trichloroethane		
0.0	39.1	1.21
4.3	35.1	1.08
11.0	33.5	1.04
21.5	33.5	1.04
39.8	32.4	1.00
Trichloroethylene		
0.0	40.7	1.19
4.3	37.2	1.09
10.0	36.4	1.06
21.5	36.2	1.06
46.1	35.2	1.03

3.3. Relation of adsorbate polarity to adsorption

Adsorption onto oven-dried soil is a function of available surface area and adsorbate molecular dimensions. Adsorption capacity is relatively constant at approximately $12 \text{ m}^2/\text{kg}$ dry soil for dipole moments varying from 0 to 1.8. At a relative humidity of 4.3 (ml water/100 ml void space), adsorption capacity for the chlorinated hydrocarbons is less and varies linearly from 2 to $6 \text{ m}^2/\text{kg}$ dry soil. At higher relative humidities, i.e. 11, 21.5 and 46.1 ml water/100 ml void space, adsorption capacity is $0\text{--}2 \text{ m}^2/\text{kg}$ dry soil at zero dipole moment and increases slightly with increasing dipole moment.

Adsorption capacities for CT and 1,2-DCA, with dipole moments of 0 and 1.83, were calculated at several soil moisture contents. Coverage declines rapidly with moisture content from the $12 \text{ m}^2/\text{kg}$ dry soil observed for oven-dried adsorbate. The effect of polarity is greatest at low moisture contents, i.e. approximately 1 g water/100 g dry soil. At higher soil moisture contents, the effect of dipole moment is small compared to the blocking effect of water on chlorinated hydrocarbon adsorption.

3.4. Adsorption isotherms

Adsorption isotherms for five chlorinated hydrocarbons are described as function of reduced solvent vapor pressure and soil moisture content in Figs. 3 and 4. Adsorbed solute concentrations have been normalized to adsorbate molecular dimensions to better represent interactions at fixed available surface area.

Inflections in the isotherms for 1,2-DCA and 1,1,1-TCA at 1.1 g water/100 g dry soil suggest that capillary condensation occurs at a p/p_{sat} of approximately, 0.4 (see Fig. 4). The compounds are polar and condense at the water interface in intra-particle pores. Compounds with lesser dipole moments appear to be too hydrophobic to condense at these interfaces.

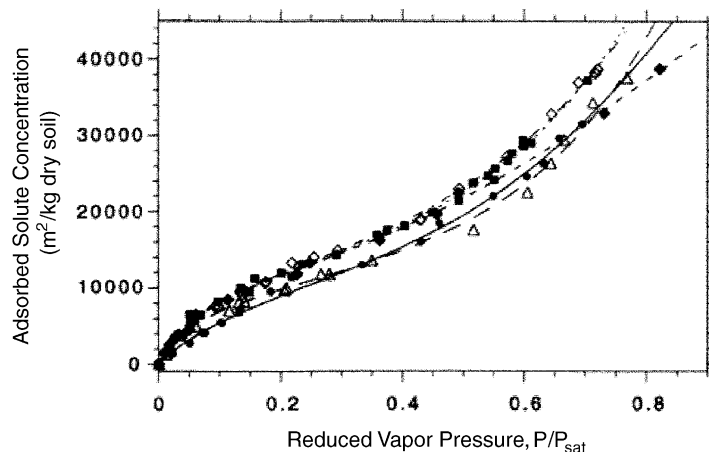


Fig. 3. Adsorption isotherms for chlorinated hydrocarbons on oven-dried Adelphia soil. Key: (●) 1,2-Dichloroethane; (△) 1,1,1-trichloroethane; (◆) trichloromethane; (◇) trichloroethylene; (■) carbon tetrachloride.

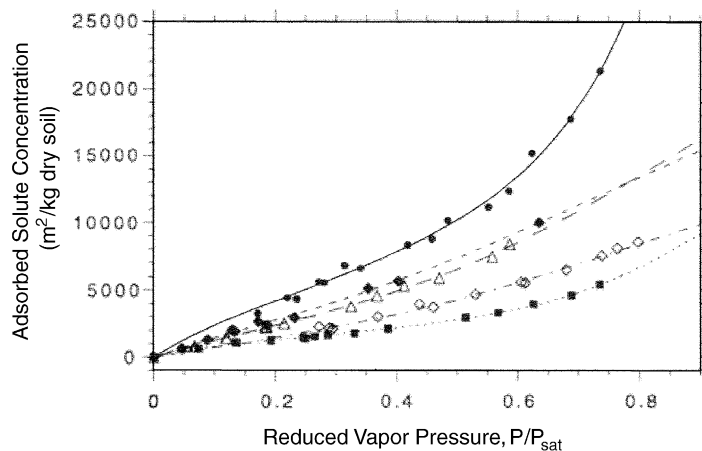


Fig. 4. Adsorption isotherms for chlorinated hydrocarbons on Adelphia soil (1.1 g water/100 g dry soil). Key: (●) 1,2-Dichloroethane; (△) 1,1,1-trichloroethane; (◆) trichloromethane; (◇) trichloroethylene; (■) carbon tetrachloride.

For the chlorinated species studied, adsorption capacity decreases with increasing molecular size. As described in Fig. 4, adsorption of TCM exceeds that of 1,1,1-TCA at reduced vapor pressures above 0.2. There are two possible contributions to this phenomenon: (i) smaller pores are accessible to TCM but not 1,1,1-TCA and (ii) the concentration of TCM adsorbed at the water/vapor interface is increased due to the high aqueous solubility of TCM. Unlike adsorption isotherms at low soil water contents, isotherms for soil moisture contents approaching field status are generally identical; CT is the exception. Adsorption isotherms for CT on moist Adelphia soil are essentially linear at all experimental moisture contents. CT has the lowest aqueous solubility of all chlorinated one- and two-carbon species and has the least effect on the surface tension of an adsorbed film of water. Surface tensions at curved interfaces are greater than surface tensions at flat interfaces and contribute to the adsorption of organic vapors [24]. Thus, the behavior of CT is consistent with its physical chemical properties.

4. Summary

New measurements of adsorption equilibria for chlorinated hydrocarbons on an unsaturated sandy loam, at various moisture contents, are reported. Experimental data have been fit by non-linear regression to a modified BET adsorption isotherm. By analogy to the BET model, simulation parameters represent apparent equilibrium coefficients and multi-layer coverage.

5. Conclusions

New equilibrium data have been obtained for binary systems of water and chlorinated hydrocarbons sorbed onto soil. Five one- and two-carbon hydrocarbons have similar isotherms

for adsorption onto oven-dried soil. In the absence of sorbed water, sorptive interactions are related to surface (soil) properties and depend weakly on sorbate (solvent) properties. At increased moisture concentrations, sorption isotherms are shifted to lesser masses of solvent bound to soil surfaces. Adsorption correlates with sorbate type, it is a non-linear function of molecular cross-section.

A modified BET adsorption isotherm represents the binary data precisely. Regression parameters correspond to apparent equilibrium coefficients and multi-layer coverage. In the absence of water, solvent molecules interact with high energy surface sites with minimal reference to molecular properties. Experimental data and simulated isotherms suggest that water molecules aggregate at surface sites with high excess surface energy, denying availability to solvent molecules and reducing weakly polar (organic) phase sorption.

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