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Received for review May 6, 1991. Revised manuscript received September 18, 1991. Accepted November 7, 1991. We are grateful to Rijkswaterstaat, Dienst Getijdewateren (The Netherlands) for their financial support under grants NOMIVE*2 No. DGW-920 and No. DGW-217.

Vapor-Phase Sorption of *p*-Xylene and Water on Soils and Clay Minerals[†]

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■ The competitive adsorption of *p*-xylene and water vapors on soil materials was studied to elucidate the mechanisms responsible for vapor-phase sorption in the unsaturated zone. Isotherms obtained from the adsorption of *p*-xylene vapors on oven-dried silica gel, kaolinite, and Webster soil were nonlinear over the range of relative vapor pressures investigated. Increasing the relative humidity to 67 and 90% resulted in dramatic reductions in *p*-xylene sorption and a shift to isotherms that were linear at *p*-xylene relative vapor pressure below 0.5. Estimates of *p*-xylene sorption based on partitioning into organic carbon did not account for the sorption of *p*-xylene on sorbents of low organic carbon content and at relative vapor pressures greater than 0.5. Dissolution of *p*-xylene into adsorbed water films was found to be insignificant at 67 and 90% relative humidity. In contrast, the adsorption of *p*-xylene at the gas-liquid interface, predicted by the Gibbs equation, contributed significantly to *p*-xylene sorption in the presence of water vapor. These findings indicate that the sorption of nonpolar organic vapors by hydrated soil materials should be described using a multimechanistic approach, which incorporates adsorption on mineral surfaces, adsorption at the gas-liquid interface, dissolution into adsorbed water, and partitioning into soil organic matter.

Introduction

Vapor-phase sorption is one of the most important factors governing the mobility and distribution of volatile organic chemicals (VOCs) in the unsaturated zone. Previous studies have demonstrated that oven-dried soils and clay minerals have a sizable capacity to adsorb organic vapors, which is strongly correlated to adsorbent surface area as determined by the Brunauer-Emmett-Teller (BET) model (1-6). Under natural conditions, the sorption of organic vapors usually occurs on surfaces containing at least some adsorbed water. As the soil moisture content or relative humidity (RH) increases, VOCs are displaced from adsorbent surfaces, resulting in the suppression of vapor-phase sorption (1, 2, 6-9). It is generally agreed that water molecules, because of their polar nature, effectively compete with nonpolar organic vapors for adsorption sites, such as exchangeable metal cations (6-9).

Although the effect of water on the extent VOC sorption is well-established, the specific mechanisms responsible for the sorption of organic vapors at relative humidities above which the sorbent surface is occupied by at least a monolayer of water remain unclear. It has been postulated that hydrated soils behave as a dual sorbent for organic vapors, in which soil organic matter functions as a partition medium and mineral surfaces function as conventional solid adsorbents (2). On the basis of the linear nature of benzene and chlorobenzene vapor sorption isotherms obtained for Woodburn soil (1.9% organic matter) at ~90% RH, and the similarity between the magnitude of solute uptake from the aqueous and vapor phases, Chiou and Shoup (2) considered partitioning into soil organic matter to be the dominant mechanism governing vapor-phase sorption under these conditions. In contrast, Call (1) attributed the sorption of ethylene dibromide (EDB) vapors on moist soils and clay minerals to adsorption at the gas-liquid interface and dissolution into adsorbed water films. Vapor-phase adsorption on the surface of bulk water has been reported for several VOCs, including benzene, toluene, and xylene (10-12). In addition, Karger et al. (13, 14), using gas chromatography methods, demonstrated that aromatic hydrocarbons and other weakly polar solutes are simultaneously adsorbed at the gas-liquid interface and dissolved into the liquid phase of water-coated support materials. For sparingly-soluble VOCs, such as *p*-xylene, the magnitude of vapor-phase sorption on soils is usually far greater than can be attributed to dissolution into adsorbed water films (7). However, due to the large surface area to volume ratio of adsorbed water films, adsorption at the gas-liquid interface of hydrated soil and clay minerals may contribute significantly to the sorption of organic vapors in the unsaturated zone.

The objective of this study was to ascertain the contribution of the following mechanisms to the sorption of *p*-xylene vapors: (a) partitioning into soil organic matter, (b) adsorption at the gas-liquid interface, (c) dissolution into adsorbed water films, and (d) adsorption on mineral surfaces. An analytical technique that allowed the amount of sorbed water and *p*-xylene to be measured independently was utilized to investigate the competitive sorption of *p*-xylene and water vapors on soil materials. Our evaluation of vapor-phase sorption mechanisms involved the comparison of measured *p*-xylene sorption data to values predicted from independent measurements of *p*-xylene sorption from the aqueous phase, the aqueous solubility of *p*-xylene, and the adsorption of *p*-xylene at

[†] Approved for publication as Florida Agricultural Experiment Station Journal Series No. R-01738.

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Table I. Physical and Chemical Characteristics of Sorbents Used To Study the Sorption of *p*-Xylene and Water Vapors

sorbent	organic carbon, g/kg	N ₂ /BET surface area, m ² /g	cation-exchange capacity, cmol/kg	particle size, g/kg			clay mineralogy
				sand	silt	clay	
kaolinite ^a	0.65 (±0.02)	13.6	4.23 (±0.03)	0	150	850	kaolinite
silica gel ^a	0.45 (±0.08)	238.0					amorphous
Webster soil	41.36 (±0.23)	2.6	51.11 (±0.53)	550	200	250	smectite, kaolinite, mica
Webster HP	2.27 (±0.09)	33.0	31.89 (±0.12)	550	200	250	smectite, kaolinite, mica

^a Adapted from Rhue et al. (7).

the gas-liquid interface estimated from the change in surface tension of bulk water with the partial pressure *p*-xylene, using the Gibbs adsorption equation. The effect of sorbent surface area and organic carbon content on the relative importance of these sorption mechanisms for a range of relative humidities is discussed.

Materials and Methods

Sorbents. The sorbents used in this study were selected to provide a range of surface area and organic carbon content. Colloidal kaolin (K-6, Lot no. 731063) was obtained from Fisher Scientific Products. The kaolinite had a cation-exchange capacity (CEC) of 4.23 cmol/kg at pH 5.5 and was predominantly Na-saturated with only trace amounts of Ca, K, and Mg (7). Silica gel (Syloid 244), average particle size of 3 μm and pore volume of 1.4 cm³/g, was obtained from the Davison Chemical Division, W.R. Grace & Co., Baltimore, MD. The Webster soil, a silty clay loam (Typic Haplaquoll), was collected from the surface horizon (0–30 cm) of a site in Iowa and ground to pass a 106-μm mesh screen. The Webster soil had a CEC of 51.11 cmol/kg and was predominantly Ca-saturated. A portion of the Webster soil (Webster HP) was treated with hydrogen peroxide buffered at pH 5.0 with acetic acid to remove organic carbon. Organic carbon content was measured by the Wakley-Black heat-of-dilution method (15). The sorbent surface areas were determined from N₂ adsorption isotherms (Advanced Materials Research Center, University of Florida). Cation-exchange capacity was determined by washing the sorbents with 1.0 M CaCl₂ five times, removing excess salt with 95% ethanol until a negative chloride test was achieved, and extracting Ca with 0.5 M Mg(NO₃)₂. The amount of Ca present in the Mg(NO₃)₂ extract was then measured by atomic absorption spectroscopy. These and other chemical and physical properties of the sorbents are presented in Table I.

Vapor-Phase Sorption Studies. Vapor-phase sorption of *p*-xylene was determined at 0 and 90% RH on Webster soil and Webster HP, and at 0 and 67% RH on kaolinite and silica gel. The flow-equilibration apparatus used to measure *p*-xylene and water vapor sorption was similar to that described in previous studies (6, 7) except for the addition of two gas-washing bottles arranged in series; the first contained water and the second contained *p*-xylene and water (Figure 1). By adjusting the three needle valves, the relative humidity could be maintained at either 67 or 90% while the *p*-xylene relative vapor pressure (P/P_0) could be varied from 0 to 0.9, where P is the equilibrium vapor pressure and P_0 is the saturated vapor pressure. The value of P_0 for *p*-xylene at 24 °C is 8.14 mmHg, which is equivalent to a vapor concentration of 46.64 mg/L (16). For the sorption experiments conducted at 0% RH, valve V_3 was closed and valves V_1 and V_2 were adjusted to obtain *p*-xylene relative vapor pressures ranging from 0 to 0.9.

The concentration of water and *p*-xylene in the flow stream was determined by passing the flow stream through three polyethylene tubes arranged in series. The three tubes contained magnesium perchlorate, activated char-

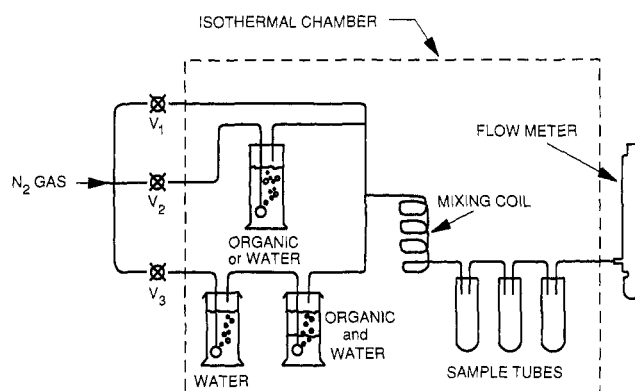


Figure 1. Flow-equilibration apparatus used to study the sorption of *p*-xylene and water vapors on silica gel, kaolinite, Webster soil, and Webster HP.

coal, and a mixture of activated charcoal and magnesium perchlorate, respectively. The difference between the initial and final trap weights yielded the total mass of vapor in the flow stream. The *p*-xylene vapor concentration was then determined by bubbling the flow stream through two 40-mL glass centrifuge tubes containing 20 mL of methanol. *p*-Xylene trapped in these solutions was measured with a Perkin-Elmer Model 320 UV-vis spectrophotometer. The concentration of water vapor in the flow stream was then determined by subtracting the concentration of *p*-xylene from the total vapor concentration.

Approximately 1 g of sorbent, which had been oven-dried at 130 °C, was placed in glass centrifuge tubes and capped with Teflon-backed septa. Four tubes containing sorbent and four blank tubes were placed on the flow stream in series. The gas flow stream passed through the centrifuge tubes via hypodermic needles at a rate of approximately 1.0 mL/s. Preliminary studies indicated that there was no significant difference in *p*-xylene sorption on samples equilibrated for 24, 48, and 96 h. In general, the system was allowed to equilibrate for at least 48 h.

Adsorbed concentrations of water and *p*-xylene were measured by extracting the sorbents with 20 mL of methanol containing CaCl₂. The methanol solution was made by adding 10 mL of CaCl₂-saturated methanol per 1 L of methanol. Water in the methanol extract was measured by Karl Fisher (KF) titration. The KF reagent was diluted with KF diluent to a strength of approximately 0.5 mL of titer per milligram of water. The visual end point was established by adding titer to 20 mL of CaCl₂-methanol solution until the desired end point was obtained. In a second centrifuge tube, 5 mL of methanol solution was pretitrated to the visual end point, and 10 μL of deionized water was injected and titrated to the end point to give the exact strength of the titer. A known volume of the methanol extract was titrated in a similar manner to determine the amount of adsorbed water.

The concentration of *p*-xylene in the methanol extract of kaolinite and silica gel was measured by UV-vis spectroscopic methods. The Webster soil and Webster HP

released methanol-soluble compounds that interfered with direct UV spectroscopic analysis. Therefore, *p*-xylene extracted from these sorbents was analyzed by standard reversed-phase liquid chromatography (RPLC) techniques using a fixed wavelength of 267 nm and a 60:25:15 eluent mixture of acetonitrile, methanol, and water, respectively. The HPLC system consisted of a Gilson 302 pump, Waters 450 UV detector, Hewlett-Packard 3392A integrator, and a 10-cm Waters RCM C-18 column with a 3-cm Brownlee guard column (17).

Aqueous-Phase Sorption Studies. Aqueous-phase sorption experiments were conducted using 5-mL glass vials equipped with open screw caps and Teflon-backed septa. Approximately 2 g of Webster soil or 3 g of Webster HP was weighed into sample vials to which 0.01 N CaCl₂ was added, followed by the addition of 0.01 N CaCl₂ saturated with *p*-xylene until there was no headspace in the vials. For kaolinite and silica gel, approximately 3 g of sorbent was added incrementally to vials containing 0.01 N CaCl₂, which were vortexed between each addition to ensure that the sorbent was completely wetted prior to the addition of 0.01 N CaCl₂ saturated with *p*-xylene. Sample vials were placed on a rotary shaker and allowed to equilibrate for ~20 h. The aqueous phase was then separated by centrifugation at 400 RCF for ~1 h using a DuPont Sorvell RT 6000 centrifuge. Reversed-phase liquid chromatography techniques were employed to determine the solution-phase concentration of *p*-xylene as described previously (17).

Surface Tension Measurements. The surface tension of distilled water exposed to *p*-xylene vapors was measured using the "drop-weight" method. The technique is based on Tate's law, which considers the weight of a drop falling from a small diameter tube to be proportional to the radius (*r*) of the tip and the surface tension (γ) of the liquid:

$$\text{weight per drop} = mg = 2\pi r\gamma \quad (1)$$

where *m* is the mass of the drop and *g* is the acceleration due to gravity. Tate's law assumes that a spherical drop will form at the tip, but in reality the drop tends to elongate before it detaches from the tip. Harkins and Brown (18) recognized the importance of this discrepancy and developed a correction factor (CF) which is a function of the ratio of the tip radius to the length of the drop:

$$CF = f(r/V^{1/3}) \quad (2)$$

where *V* is the volume of the drop. In general, the values of $r/V^{1/3}$ ranged from 0.45 to 0.5, which correspond to a CF of 0.6669–0.6515, respectively (18). The following equation was then used to calculate the surface tension:

$$\gamma = mg/2\pi rCF \quad (3)$$

A 10-mL graduated buret was used to measure the surface tension of deionized water and *p*-xylene solutions. After the tip was carefully ground flush, an ocular microscope was used to measure the diameter of the tip (0.37 cm). Drops falling from the tip of the buret were collected in a 40-mL centrifuge tube capped with a Teflon-backed septa. A 0.4-cm-diameter hole was cut in the septa, and the height of the centrifuge tube was adjusted to achieve a tight seal between the septa and the buret. A total of 18–20 drops, at a rate of 4–6 drops per minute, were collected in the centrifuge tube. The volume and weight of drops collected were then used to calculate the surface tension of liquid. Solutions of NaCl were used to calibrate the diameter of the tip (0.3724 cm).

p-Xylene vapor, at relative vapor pressures ranging from 0.1 to 0.8, was bubbled through a 50-mL centrifuge containing approximately 40 mL of deionized water. No de-

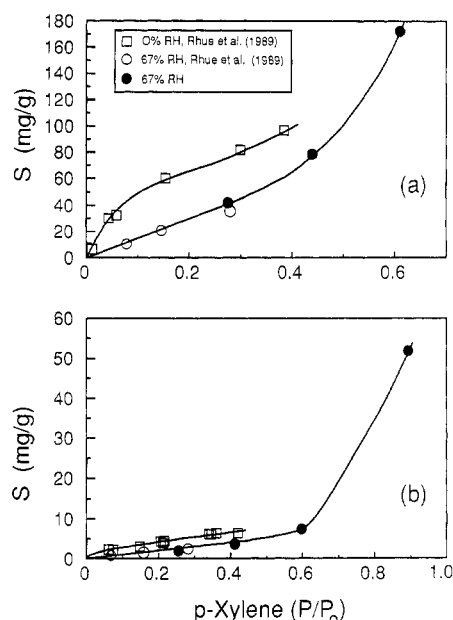


Figure 2. Sorption of *p*-xylene vapors on (a) silica gel and (b) kaolinite at 0 and 67% RH.

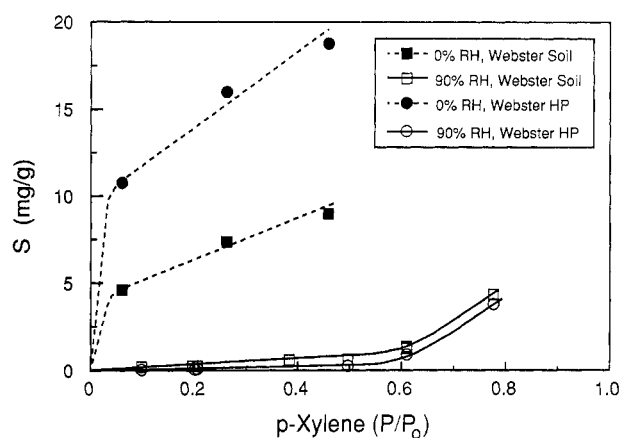


Figure 3. Sorption of *p*-xylene vapors on Webster soil and Webster HP at 0 and 90% RH.

tectable change in the *p*-xylene concentration was measured after 24, 48, and 96 h of bubbling. Therefore, the system was allowed to equilibrate for at least 24 h. The surface tension of distilled water exposed to *p*-xylene vapors was determined in the same manner as described previously, except that the *p*-xylene vapor was allowed to flow through the collection tube for at least 2 min prior to initiating the flow of drops.

Results and Discussion

Adsorption at 0% Relative Humidity. Figures 2 and 3 show equilibrium isotherms for the sorption of *p*-xylene vapors on oven-dried silica gel, kaolinite, Webster soil, and Webster HP at 24 °C. Sorption data are expressed as milligram of *p*-xylene sorbed per gram of sorbent (*S*) versus the *p*-xylene relative vapor pressure (*P*/*P*₀). At 0% RH, *p*-xylene adsorption on all four sorbents corresponded to type-II BET isotherms, which is characteristic of unrestricted monolayer-multilayer adsorption on nonporous or macroporous (pore width >0.05 μm) sorbents (19). However, the possibility exists that silica gel could exhibit hysteresis and limiting sorption at high values of *P*/*P*₀ due to capillary condensation of *p*-xylene in mesopores, resulting in a type-IV isotherm. In either case, the BET model can be utilized to obtain the nominal monolayer sorption capacity (*S*_m) and the value of *C*, a parameter

Table II. Brunauer–Emmett–Teller Parameters Calculated from Single-Sorbate Sorption Isotherms

sorbent	sorbate	S_m , mg/g	C	BET surface area, m^2/g	P/P_0 monolayer	P/P_0 range used
kaolinite ^a	<i>p</i> -xylene	4.5	14	15	0.21	0.065–0.424
	water	4.2	20	10	0.18	0.056–0.481
silica gel ^a	<i>p</i> -xylene	64.7	17	139	0.20	0.003–0.387
	water	33.8	18	119	0.18	0.027–0.348
Webster soil	<i>p</i> -xylene	5.7	48	12	0.13	0.061–0.264
Webster HP	<i>p</i> -xylene	12.3	73	27	0.10	0.061–0.262

^a Adapted from Rhue et al. (7).

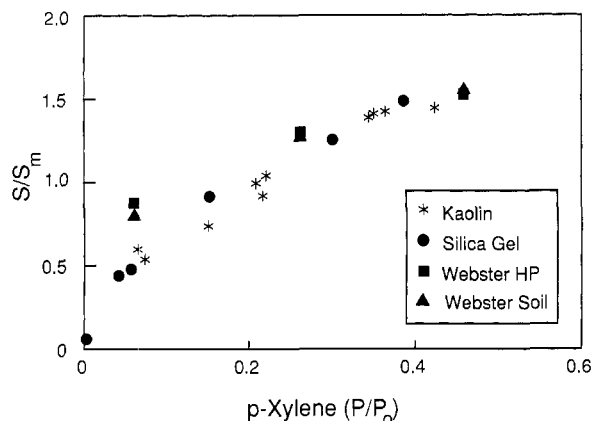


Figure 4. Sorption of *p*-xylene vapors on silica gel, kaolinite, Webster soil, and Webster HP at 0% RH, normalized to the value of S_m determined from the BET equation.

related to the heat of adsorption (19). Thus, the sorption data were fit by a least-squares procedure to the following linear form of the BET equation:

$$\frac{P/P_0}{S(1 - P/P_0)} = \frac{1}{S_m C} + \frac{(C - 1)P/P_0}{S_m C} \quad (4)$$

Estimated values of S_m and C and the values of P/P_0 associated with the monolayer coverage of *p*-xylene are presented in Table II.

A relative sorption term (S/S_m) was employed to compare the sorptive capacity of oven-dried kaolinite, silica gel, Webster soil, and Webster HP on a unit-surface area basis (Figure 4). At low values of P/P_0 , the relative sorption of *p*-xylene on Webster HP and Webster soil was slightly greater than that on kaolinite and silica gel. The increased sorption capacity of Webster soil and Webster HP corresponded to larger values of C , which suggests that specific sorbate–sorbent interactions may have occurred. However, the overall similarity in the relative sorption isotherms is remarkable given the disparity in the OC content and surface area of the sorbents and suggests that the sorption of *p*-xylene vapors at 0% RH is primarily a function of surface area.

The surface area available for the adsorption of a given molecule can be estimated from the value of S_m and the area occupied by each adsorbed molecule. The cross-sectional area of water and *p*-xylene was calculated to be 0.105 and 0.380 nm², respectively, using the following equation:

$$a_m = 1.09(MW/\tau A)^{2/3} \quad (5)$$

where MW is the molecular weight, τ is the liquid density, and A is Avogadro's number (20, 21). This equation assumes that the sorbate molecules are oriented in a hexagonal close packing at a density similar to that of the bulk liquid. The BET surface areas calculated from *p*-xylene and water adsorption at monolayer coverage (S_m) are shown in Table II.

It is widely recognized that N₂ adsorption provides a measure of the external surface area of clay minerals (22) and soil organic matter (23), whereas polar molecules such as ethylene glycol penetrate into interlayer surfaces, thereby providing a measure of total surface area (22). The *p*-xylene/BET surface areas of kaolinite, Webster soil, and Webster HP were similar to those derived from N₂ adsorption isotherms (Table I). These data are consistent with the findings of Call (1) and Rhue et al. (7), who reported that the BET surface area of soils and clay minerals determined from the adsorption of nonpolar organic vapors, such as *p*-xylene, toluene, and ethylene dibromide (EDB), was almost identical to the corresponding N₂/BET surface areas. These data suggest that nonpolar organic vapors are adsorbed on the external surfaces of anhydrous soils and clay minerals in much the same manner as N₂ molecules.

The treatment of Webster soil with hydrogen peroxide to remove soil organic matter increased both the *p*-xylene and N₂/BET surface areas from 12 to 27 m²/g and from 2.6 to 33.0 m²/g, respectively. A similar response was observed for Whittlesey Black Fen soil (16.4% organic carbon), the EBD and N₂/BET surface areas of which increased from 17.5 to 50.5 m²/g and from 12.7 to 71.0 m²/g, respectively, following a hydrogen peroxide treatment (1). These data demonstrate that the sorption of nonpolar organic vapors on anhydrous soil materials is primarily the result of adsorption on mineral surfaces rather than uptake by soil organic matter. The values of C , derived from the *p*-xylene adsorption isotherms for Webster soil ($C = 38$) and Webster HP ($C = 72$), also suggest that *p*-xylene vapors have a greater affinity for mineral surfaces than for soil organic matter (Table II). The surface area of Whittlesey Black Fen soil, based on both the retention of ethylene glycol and the adsorption of water vapor, actually decreased after the hydrogen peroxide treatment. These data support the theory that polar molecules explore the total surface area of clay minerals and soil organic matter, while the adsorption of nonpolar organic vapors and N₂ is limited to external surfaces. The discrepancy between the N₂ and *p*-xylene/BET surface area of silica gel has been discussed in a previous paper (7).

Sorption at 67 and 90% Relative Humidity. Vapor-phase sorption of *p*-xylene on kaolinite and silica gel was substantially reduced when the relative humidity was raised to 67% (Figure 2). The observed suppression of vapor-phase sorption at 67% RH is consistent with the reported heats of adsorption for water and organic vapors on mineral surfaces. Jurinak and Volman (24) found that the initial heat of water adsorption on Ca- and Ba-saturated kaolinite was approximately –120 kJ/mol. In contrast, Rao et al. (5) reported heats of adsorption for trichloroethylene (TCE), toluene, and cyclohexane vapors on Oldsmar soil of –23, –37, and –34 kJ/mol. Thus, as the relative humidity increases, water effectively competes with organic vapors for mineral adsorption sites, resulting in

Table III. Partition Coefficients Normalized to Sorbent Organic Carbon Content (K_{oc}) Derived from Vapor-Phase Sorption Data and Batch Aqueous-Phase Sorption Experiments

sorbent	RH, %	OC content, g/kg	K_d , mL/g	K_{oc} , mL/g	
				predicted	measured
silica gel	67	0.45	1.53 (± 0.13)	1.684×10^6	3.400×10^3
kaolinite	67	0.65	0.28 (± 0.02)	7.486×10^4	4.292×10^2
Webster HP	90	2.27	1.03 (± 0.04)	1.203×10^3	4.533×10^2
Webster soil	90	41.36	3.10 (± 0.09)	1.764×10^2	7.495×10^1

the suppression of VOC sorption. This hypothesis is supported by spectroscopic investigations of vapor-phase sorption, which have demonstrated that *p*-xylene chemisorbed on Cu-saturated montmorillonite is almost completely removed from the clay surface following exposure of the *p*-xylene-clay complex to water vapor (25). The sorption of *p*-xylene vapors on Webster soil and Webster HP was also reduced dramatically in the presence of water vapor (Figure 3). However, the sorptive capacity of Webster soil at 90% RH was greater than that of Webster HP, while the reverse was true at 0% RH. These data suggest that partitioning into soil organic matter contributed to *p*-xylene sorption at 90% RH, whereas adsorption on mineral surfaces was the dominant mechanism at 0% RH.

The presence of water vapor not only reduced *p*-xylene sorption but also resulted in a shift from type-II to type-III adsorption isotherms. The linear nature of the sorption isotherms below $0.5 P/P_0$ is consistent with the isotherms obtained by Call (1) for EDB sorption on hydrated Camontmorillonite and by Chiou and Shoup (2) for benzene and chlorobenzene sorption on Woodburn soil at $\sim 90\%$ RH. Type-III adsorption isotherms are characteristic of weak gas-solid interactions, and thus the conversion of a type-II to a type-III adsorption isotherm can be achieved by reducing adsorbate-adsorbent interactions. Kiselev (26) treated a hydroxylated silica gel with trimethylchlorosilane to replace the hydroxyl groups with nonpolar $\text{Si}(\text{CH}_3)_3$ groups. As the concentration of $\text{Si}(\text{CH}_3)_3$ groups on the surface was increased, both polar and dispersive interactions between benzene vapors and the silica gel diminished, resulting in the suppression of benzene adsorption and a shift from type-II to type-III isotherms. In a similar manner, the adsorption of polar molecules, such as water, on mineral surfaces can reduce adsorbate-adsorbent interactions. For example, isotherms obtained for the adsorption butane vapors on ball-milled calcite were shifted from type-II to type-III when the calcite was covered with at least a monolayer of water (27). The adsorption of hydrocarbons on water-coated silica and soil materials, measured by gas chromatography techniques, also yields type-III adsorption isotherms (13, 14, 28, 29). These data are consistent with the adsorption of hydrocarbons on the surface of bulk water and indicate that adsorbed water films represent a low energy surface upon which organic vapors are weakly adsorbed (10-14).

Elucidation of Sorption Mechanisms. From a theoretical perspective, a number of mechanisms may contribute to vapor-phase sorption at high relative humidities, including (a) partitioning into soil organic matter, (b) adsorption on mineral surfaces, (c) dissolution into adsorbed water films, and (d) adsorption at the gas-liquid interface. Chiou and Shoup (2) considered solute partitioning into organic carbon to be the dominant mechanism governing organic vapor sorption on Woodburn soil at $\sim 90\%$ RH. This hypothesis was based primarily on two pieces of evidence: (a) the linear nature of the sorption isotherms and (b) the similarity in sorption from the aqueous and vapor phases. However, the *p*-xylene sorption data presented

in Figures 2 and 3 demonstrate that below $0.5 P/P_0$ linear isotherms can be obtained for sorbents with OC contents ranging from trace levels to 41 g/kg. Therefore, the existence of a linear isotherm is not sufficient evidence to conclude that partitioning into organic carbon has occurred. In addition, the dramatic increase in sorption above $0.5 P/P_0$ is not consistent with the partitioning theory.

To further evaluate the role of soil organic matter in vapor-phase sorption, sorption coefficients normalized to the sorbent organic carbon content (K_{oc}) were compared to values of K_{oc} estimated from measured *p*-xylene sorption data for values of P/P_0 below 0.5 (i.e., the linear portion of the isotherm) and the aqueous concentration of *p*-xylene (Table III). The concentration of *p*-xylene in the aqueous phase, estimated using a calculated K_H value of $6.086 \times 10^{-3} \text{ m}^3\text{-atm/mol}$ (30), was subtracted from the measured sorption data prior to the calculation of sorption coefficients. Measured K_{oc} values for Webster soil, Webster HP, and kaolinite were similar to those derived from column experiments (105-176 mL/g) (31, 32) and the *p*-xylene log octanol-water partition coefficient of 3.15 (573 mL/g) (33). However, the estimated *p*-xylene K_{oc} values for silica gel, kaolinite, and Webster HP and Webster soil were 495, 174, 2.7, and 2.3 times greater, respectively, than the measured values. Although the predicted K_{oc} values approached the measured values as the sorbent organic carbon content increased, these data clearly indicate that mechanisms other than or in addition to partitioning into soil organic matter contributed to *p*-xylene sorption at 67 and 90% RH.

Chiou and Shoup (2) proposed that soil functions as a dual sorbent; that is, both soil organic matter and mineral surfaces contribute to vapor-phase sorption. Thus, it is logical to attribute the discrepancy between the measured and predicted K_{oc} values to adsorption of *p*-xylene on mineral surfaces. Therefore, the sorption of *p*-xylene by the solid phase was predicted using aqueous-phase sorption coefficients (K_d) and the concentration of *p*-xylene in the aqueous phase, estimated as described previously (Table IV). Predictions of *p*-xylene sorption by kaolinite and silica gel based on the aqueous-phase sorption coefficient represented less than 1% of the measured values. In contrast, up to 38 and 46% of the *p*-xylene sorption on Webster HP and Webster soil, respectively, was accounted for by the aqueous-phase sorption coefficients. In both cases the disparity between measured and predicted sorption became considerably larger at relative vapor pressures greater than 0.6. The amount of *p*-xylene dissolved in adsorbed water films was predicted based on the measured values of water sorption and the estimated aqueous-phase concentration of *p*-xylene (Table IV). As expected, given the low aqueous solubility of *p*-xylene (198 mg/L), the quantity of *p*-xylene dissolved in adsorbed water films was insignificant relative to the total amount of *p*-xylene sorption.

The analysis presented herein demonstrates that mechanisms other than sorption by the solid phase (i.e., adsorption at the solid-liquid interface and partitioning into soil organic matter) and dissolution into adsorbed water

Table IV. Predicted and Measured *p*-Xylene Sorption on Silica Gel and Kaolin at 67% RH, and Webster HP and Webster Soil at 90% RH

sorbent	<i>P/P</i> ₀	adsorption air-liquid interface, mg/g	sorption by the solid phase, mg/g	dissolution into adsorbed water films, mg/g	total sorption, mg/g	
					predicted	measured
silica gel	0.081	1.802	0.023	0.001	1.826	11.61
	0.145	3.921	0.041	0.002	3.964	20.74
	0.274	10.052	0.078	0.003	10.133	41.95
	0.282	10.514	0.081	0.003	10.568	36.73
	0.439	21.522	0.125	0.004	21.786	80.19
	0.610	37.706	0.174	0.008	37.888	173.97
kaolinite	0.069	0.084	0.003	0.000	0.087	0.45
	0.164	0.267	0.009	0.000	0.276	1.41
	0.258	0.523	0.013	0.001	0.537	2.28
	0.286	0.614	0.015	0.001	0.630	2.77
	0.415	1.120	0.022	0.001	1.143	3.76
	0.600	2.094	0.031	0.001	2.127	7.71
Webster HP	0.896	18.262	0.047	0.001	18.310	52.19
	0.099	0.324	0.019	0.002	0.345	0.05
	0.201	0.870	0.039	0.003	0.913	0.08
	0.206	0.903	0.040	0.003	0.946	0.10
	0.497	3.677	0.095	0.009	3.781	0.28
	0.601	5.228	0.117	0.009	5.354	0.91
Webster soil	0.777	14.014	0.149	0.011	14.174	3.88
	0.099	0.026	0.057	0.002	0.085	0.21
	0.197	0.067	0.114	0.003	0.184	0.26
	0.206	0.072	0.119	0.004	0.195	0.25
	0.384	0.190	0.222	0.006	0.418	0.61
	0.497	0.292	0.288	0.010	0.590	0.63
	0.610	0.415	0.353	0.010	0.778	1.31
	0.777	1.113	0.450	0.013	1.576	4.36

films must be considered in order to account for vapor-phase sorption of *p*-xylene, particularly on sorbents of low OC content and at high relative vapor pressures. Adsorption of hydrocarbon vapors on the surface of water-coated solids and bulk water has been shown to yield type-III adsorption isotherms and thus was considered as a potential sorption mechanism. The adsorption of insoluble and sparingly-soluble hydrocarbons at the gas-liquid interface has been estimated by measuring the change in surface tension with the partial pressure of the organic vapor (10-12, 34, 35). This approach is based on the Gibbs adsorption equation:

$$\Gamma = -d\gamma/d\mu \quad (6)$$

where Γ is the surface excess, γ is the surface tension, and μ is the chemical potential. If the vapor is assumed to obey the ideal gas law, eq 6 can be written as

$$\Gamma = -(p/RT) (d\gamma/dp) \quad (7)$$

where p is the partial pressure of the organic vapor. The surface tension of distilled water exposed to *p*-xylene vapor, determined by the drop-weight method, is shown in Figure 5a. These data were fit by a nonlinear least-squares regression procedure to yield a slope which could be used to calculate the surface excess as a function of the partial pressure using eq 7 (Figure 5b). The type-III adsorption isotherm generated from this procedure is similar to those obtained for other aromatic hydrocarbons and indicates that water acts as a low-energy surface toward *p*-xylene vapors (11, 36).

The quantity of *p*-xylene adsorbed at the gas-liquid interface was estimated from the surface excess and the N_2 /BET surface area of each sorbent (Table IV). These data suggest that adsorption on the gas-liquid interface contributed significantly to *p*-xylene sorption on silica gel and kaolinite at 67% RH. In contrast, partitioning into soil organic matter matter and dissolution into sorbed water accounted for less than 1% of *p*-xylene sorption, due to the low organic carbon content of these sorbents and the low aqueous solubility of *p*-xylene, respectively. The

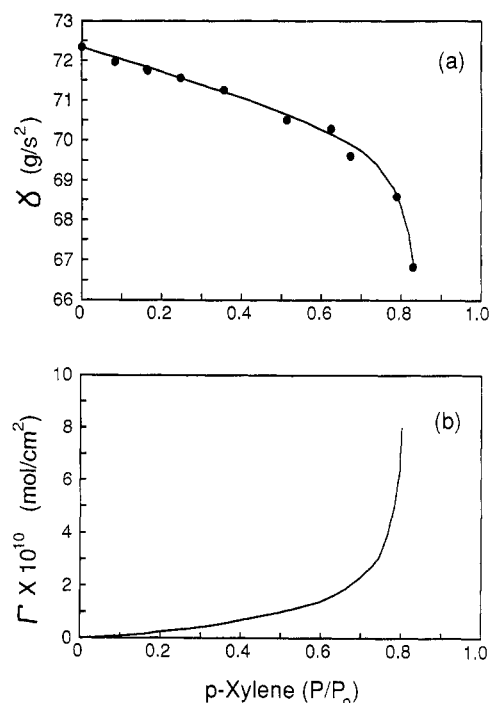


Figure 5. Surface tension (a) of deionized water exposed to *p*-xylene vapors at 24 °C measured by the drop-weight method and the surface excess (b) of *p*-xylene at the gas-liquid interface calculated using the Gibbs adsorption equation.

total predicted sorption of *p*-xylene on silica gel and kaolinite was approximately 25% of the measured amount. This discrepancy may have been due to adsorption of *p*-xylene vapors on exposed mineral surfaces or to the structuring of water adsorbed on mineral surfaces. Dorris and Gray (28) concluded that the surface of silica exerted a significant impact on hydrocarbon vapor sorption at 25.7 and 62.3% RH and suggested that bare patches of silica may have existed at these relative humidities. The average amount of water adsorbed on silica gel and kaolin at 67%

RH was 57.9 and 9.3 mg/g, respectively, which is equivalent to 1.7 and 2.2 monolayers of water, based on BET estimates of S_m (Table II). Due to the low values of C for these sorbents, it is possible that discrete patches of water formed on the mineral surface (3, 19), thereby allowing for the existence of exposed mineral surfaces. Therefore, it is plausible that additional *p*-xylene adsorption could have occurred on exposed mineral surfaces or resulted from the condensation of *p*-xylene vapors in pore spaces not occupied by water. Even if monolayer coverage of water was attained, the mineral surface could still have exerted an effect on the sorbed water film (37), resulting in greater sorption than would be predicted for bulk water surfaces. Thus, the possibility exists that the *p*-xylene surface excess present on adsorbed water films of silica gel and kaolinite at 67% RH was greater than that observed for distilled water. In contrast, water adsorbed on Webster soil and Webster HP at 90% RH is likely to exhibit properties similar to those of bulk water. Karger et al. (14) demonstrated that adsorbed water films of ~1.5–200 nm in thickness (which corresponds to water loadings of 5–40%) behave as bulk water with respect to hydrocarbon vapors. In addition, Dorris and Gray (28) reported that hydrocarbon sorption coefficients remained constant at water loadings ranging from 3.8 (88% RH) to 47% by weight. Therefore, the mechanisms governing vapor-phase sorption at 90% RH should be similar to those at field capacity, at which time the relative humidity may exceed 99%.

Predicted sorption of *p*-xylene on Webster soil at 90% RH was similar to measured values at relative vapor pressures less than 0.6. Adsorption at the gas-liquid interface and sorption by the solid phase each accounted for approximately 50% of the *p*-xylene sorption on Webster soil (Table IV). In contrast, predicted sorption of *p*-xylene at the gas-liquid interface of Webster HP was considerably greater than the measured values. Dissolution into sorbed water films and partitioning into soil organic matter contributed very little to the overall estimate of *p*-xylene sorption on Webster HP. The N_2 /BET surface area of Webster HP would have to be reduced from 33.8 m²/g to approximately 2.5 m²/g in order to bring the estimated adsorption at the gas-liquid interface into agreement with the measured sorption data. Thus, the successful prediction of *p*-xylene sorption on Webster soil may have been due, in part, to the low N_2 /BET surface area (2.62 m²/g). These data demonstrate the sensitivity of the model to variation in the surface area used to calculate adsorption at the gas-liquid interface.

Although reliable values of S_m can be obtained from the adsorption of organic vapors on anhydrous sorbents, the BET model can only be applied to isotherms which exhibit a distinct inflection point corresponding to monolayer coverage (point B). To date, no acceptable procedure has been developed to determine the surface area of water-coated or partially-hydrated sorbents. Thus, the prediction of organic vapor adsorption on the gas-liquid interface based on N_2 /BET surface areas must be considered a first-order approximation. However, the data presented herein clearly demonstrate that predictions of organic vapor sorption cannot be based solely on dissolution into adsorbed water films and sorption by the solid phase and that adsorption at the gas-liquid interface contributes significantly to vapor-phase sorption by hydrated soil materials.

Summary and Conclusions

Antecedent moisture content or relative humidity is arguably the most important factor influencing vapor-phase sorption in the unsaturated zone. In the absence

of water, soils and clay minerals exhibit a sizable capacity to adsorb *p*-xylene vapors, which is governed primarily by adsorption on mineral surfaces. However, such dry conditions are rarely encountered in nature and may only exist at the soil surface or in arid climates. When the relative humidity was increased to 67 and 90%, the sorption of *p*-xylene vapors decreased significantly and conformed to a type-III isotherm. In general, the sorption of organic vapors by hydrated soils is described by the dissolution of organic vapors into adsorbed water films, using Henry's law constants (K_H), and subsequent sorption by the solid phase, using sorption coefficients (K_d or K_{oc}) (38, 39). However, a critical evaluation of *p*-xylene K_{oc} data, sorption by the solid phase, and dissolution into adsorbed water films indicates that such an approach does not fully account for the sorption of *p*-xylene vapors by hydrated sorbents. A consideration of *p*-xylene adsorption at the gas-liquid interface, based on the Gibbs adsorption equation, suggests that this mechanism contributed significantly to *p*-xylene sorption on water-coated soil materials. This hypothesis is supported by the following evidence: (a) Type-III adsorption isotherms were obtained from *p*-xylene adsorption on sorbents at 67 and 90% RH, (b) predicted *p*-xylene adsorption at the gas-liquid interface accounted for up to 50% of the actual *p*-xylene sorption, and (c) these data are consistent with previous measurements of hydrocarbon vapor adsorption on the gas-liquid interface of water-coated solid supports.

On the basis of these findings we recommended that a multimechanistic approach, which includes (a) adsorption on mineral surfaces, (b) partitioning into soil organic matter, (c) dissolution into sorbed water films, and (d) adsorption on the gas-liquid interface, be utilized to describe vapor-phase sorption in the unsaturated zone. The relative importance of these mechanisms will depend primarily on the soil moisture content, the surface area and organic carbon content of the sorbent, and the vapor pressure and solubility of the VOC. For sparingly-soluble VOCs, such as *p*-xylene, it is probable that partitioning into soil organic matter and adsorption at the gas-liquid interface will be the dominant mechanisms contributing to vapor-phase sorption. As the aqueous solubility of the VOC increases, dissolution of organic vapors into adsorbed water films will comprise a greater proportion of the overall sorption (1, 40). The challenge now is to further characterize the contribution of each mechanism to vapor-phase sorption and incorporate this knowledge into current multiphase flow and transport models.

Acknowledgments

We thank Linda S. Lee for conducting the aqueous-phase sorption experiments.

Registry No. *p*-Xylene, 106-42-3; water, 7732-18-5.

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Received for review August 7, 1991. Accepted December 10, 1991.

Comparison of Semianalytical Methods To Analyze Complexation with Heterogeneous Ligands

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■ The binding of ions to natural ligands is influenced by the chemical heterogeneity of these ligands. Two approaches to calculate the affinity distribution are compared in terms of theory and practicality. The local isotherm approximation (LIA) methods use an approximation of the local binding function in order to solve the integral adsorption equation for the distribution function. The differential equilibrium function (DEF) method is based on the law of mass action, but it is shown that the method can also be interpreted within the LIA concept. The results obtained with the LOGA method, on the basis of accurate synthetic data on binding, are fairly good, but in general the distribution is somewhat flattened. The DEF distributions are asymmetrically distorted, but the position of a small peak at the high-affinity end of a distribution is clearly discernable.

Introduction

The binding of metal ions and other chemical species to naturally occurring polyfunctional ligands affects the bioavailability and transport of those chemical species present in natural systems. The ligands may be present as small dissolved molecules or as reactive sites at the surface of mobile or immobile colloids. Natural colloids

such as fulvic and humic acids possess different types of reactive groups; that is to say, they are chemically heterogeneous.

When the binding behavior of metal ions and other chemical species on natural ligands is studied, heterogeneity analysis is a valuable tool and may be helpful when a realistic model to describe the binding is to be chosen. Early work on the heterogeneity of polyfunctional ligands was done by researchers such as Simms (1), Scatchard et al. (2), Tanford (3), and Klotz and Hunston (4), who treated the ligand system as a discrete series of site types, and Posner (5) and Gamble (6), who considered a continuous distribution of the heterogeneity. Hunston (7) applied the work of Ninomiya and Ferry (8), who worked on the viscoelastic behavior of materials, to the binding of small molecules to macromolecules.

In the last decade, interest in the topic has increased (9-20). In the field of physical chemistry, the effect of the heterogeneity of a surface on the adsorption of small molecules has also attracted much attention; see the reviews by House (21) and Jaroniec and Bräuer (22). Both purely numerical and semianalytical methods of heterogeneity analysis have been published. In this paper we will discuss the semianalytical methods for heterogeneity analysis based on continuous distributions. This critical comparison of the numerous methods of this type of analysis may help future users to select a method. As we recently discussed the local isotherm approximation (LIA)

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