Adsorption Kinetics of Toluene on Soil Agglomerates: Soil as a Biporous Sorbent

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Single-component vapor diffusion at low pressure into dry soil agglomerates provides a well-characterized system for investigating adsorption and diffusion mechanisms. Equilibrium and kinetic data for adsorption of toluene vapor on Yolo loam and montmorillonite clay were obtained in this study with a gravimetric method. More extensive equilibrium data were obtained with a headspace gas chromatographic technique. Freundlich isotherms provided a good fit to the equilibrium data for relative partial pressures less than 0.6. Adsorption of toluene from the gas phase occurred in two stages: the first was due to fast diffusion and adsorption in macropores, and the second was controlled by slower diffusion and adsorption in intragrain micropores. As several days are required to establish equilibrium, the effect of slow diffusion and adsorption would be overlooked in shorter studies. Numerical simulations described the isothermal adsorption of toluene on spherical soil particles subject to a step change in bulk concentration. Biporous diffusion models are necessary to interpret the distinct diffusional characteristics of toluene in macropores and micropores with nonlinear adsorption. The simulations quantitatively describe details of the adsorption history.

Introduction

The description of transport processes in soil is inherently difficult because of the heterogeneous composition of the soil surfaces and the complex nature of the pore network. Volatile organic compounds (VOCs) can absorb into soil organic matter (SOM) and adsorb on soil mineral surfaces. Models of transport of volatile organic compounds (VOCs) in contaminated soil include sorption kinetics (1, 2) and diffusion processes (3–6). A review of mass transfer and diffusion models can be found in Brusseau and Rao (7), and an overview of kinetics models is in Connaughton et al. (1). Because most soils are aggregates of heterogeneous grains with a broad range of pore sizes, diffusion mechanisms will be significant in describing VOC transport. In the present study, both the influences of diffusion and adsorption on VOC mass transfer are addressed. Since water is a strong competitor for soil adsorption sites, VOC adsorption on dry soil is up to 100 times higher than in moist saturated grains (8). Dry and low SOM content soil samples were used to clarify the role of diffusive transport in the soil pore network and adsorption at mineral surfaces.

Lin et al. (3) applied a homogeneous, porous-sphere diffusion model to describe the effect of nonlinear sorption on the intraparticle diffusion of VOCs in dry soil particles. The model predicted the adsorption trend, but was unable to describe the adsorption history details at longer times. In the early stages of the present work, a similar model was extended to take into account the boundary layer resistance at the sorbent outer surface. The model failed, however, to describe the adsorption behavior at longer times, showing the inadequacies described by other investigators (3, 9–11). This suggested that an additional rate process was operating.

Soil agglomerates have large pores (macropores) due to spaces between the (clay, silt and sand) particles and have small pores (micropores) in the internal structure of the particles themselves. Sometimes the particles are individual grains (as in sands), but usually they are clustered together as aggregates (12). Between and within particles, an intricate pore network provides the surface for adsorption. The IUPAC pore classification divides pores into three categories based on their size: micropores d < 20 Å, mesopores 20 Å < d < 500 Å, and macropores d > 500 Å (13). Micropores are sometimes referred to as adsorbing pores, and the last two varieties are combined under the common classification of transport pores (10). When the pore size approaches the magnitude of the adsorbate mean free path, Knudsen diffusion becomes the predominant transport mechanism. The diffusional time constant (D/ r²) for the micropore structure in microparticles of radius (r) can differ by several orders of magnitude from mesopores to macropores. In very small pores, due to the proximity of the pore wall, steric effects are important in reducing diffusion. Diffusion and adsorption in micropores are suggested to cause slow aqueous elution of VOCs and pesticides from soil samples (14–17).

The actual pore structure of a sorbent can often be approximated as independent averages of two pore-size ranges, representing macropores and micropores, where two different diffusional mechanisms operate (11). Such biporous sorbents include ion exchange resins (18), heterogeneous catalysts (19), and industrial adsorbents (20). Most synthetic and natural solid sorbents, such as activated carbon and soil, exhibit pores in both diffusion ranges, i.e., macropores and micropores, so that a biporous adsorption–diffusion model is appropriate to describe their sorption rate behavior.

In early work, Ruckenstein et al. (18) considered microspheres embedded in a macrophere as an idealized geometry for linear adsorption and diffusion into ion-exchange resins. The same problem was considered later by Ma and Lee (21) and Lee (22), who extended the linear model to describe a system with a finite volume of external fluid. Doong and Yang (20) simplified a linear adsorption bidisperse pore diffusion model by assuming parabolic concentration profiles for micropore and macropore zones. More recently, Peterson (23) analytically solved the transport...
Biporous-Sphere Diffusion Models for Adsorption

We are interested in modeling adsorbate uptake as a function of radial position ($r$) and time ($t$) for spherical soil agglomerates initially at equilibrium with gas-phase VOC concentration ($C_o$). At $t = 0$, the sample is subject to a step change in bulk concentration, which is maintained constant during adsorption. The schematic drawings for the proposed models are shown in Figure 1. The last three models in Figure 1 assume a bidisperse (macropore and micropore) structure. The models are simplified by the assumption of local equilibrium at the gas-solid interface, i.e., the rates of adsorption and desorption are fast relative to other rate processes. Model refinements showed that the mass transfer resistance due to the concentration boundary layer outside the particles was negligible. Simplifications applied to the models presented in this work are shown for the microspheres inside a macrosphere biporous model. Similar algebraic manipulations apply for all models. The governing differential equations and the solution details are given by Arocha (30).

The microspheres-in-macrosphere model shown in Figure 1C was originally developed by Ruckenstein et al. (18). Here, we extend this model to account for nonlinear adsorption. The soil is pictured as large spherical aggregates of small microporous spheres of uniform size. The micropores are exclusively contained in the microspheres, while the macropore spaces are the interstices between the microspheres. The soil clay fraction, made up of particles less than 2 µm in diameter (31), contains most of the micropores in the soil matrix and adsorbs VOCs strongly.

The governing differential equations are provided in Table 1. Adsorption and diffusion in a biporous system are
TABLE 1
Governing Differential Equations with Initial and Boundary Conditions for Microspheres inside a Macropore Biporous Model

in macropores
$$\epsilon_a \frac{D_a}{\tau} \frac{\partial C_a}{\partial t} + S_a \frac{\partial C_a}{\partial \xi} = D_a \frac{\partial^2 C_a}{\partial x^2} - \eta \text{pr} R \frac{\partial C_a}{\partial \eta}$$ (1.1)

in micropores
$$\frac{D_{a,p}}{\tau} \frac{\partial C_{a,p}}{\partial t} + S_{a,p} \frac{\partial C_{a,p}}{\partial \xi} = \frac{D_{a,p}}{\tau} \frac{\partial^2 C_{a,p}}{\partial x^2}$$ (1.2)

The dimensionless forms:

in macropores
$$\frac{D_a}{\tau} \frac{\partial C_a}{\partial t} + S_a \frac{\partial C_a}{\partial \xi} = D_a \frac{\partial^2 C_a}{\partial x^2} - \eta \text{pr} R \frac{\partial C_a}{\partial \eta}$$ (1.3)

in micropores
$$\frac{D_{a,p}}{\tau} \frac{\partial C_{a,p}}{\partial t} + S_{a,p} \frac{\partial C_{a,p}}{\partial \xi} = \frac{D_{a,p}}{\tau} \frac{\partial^2 C_{a,p}}{\partial x^2}$$ (1.4)

With transformations, U(x,0) = xc(x,0) and W(y,0) = yc(x,y,0) in macropores
$$\frac{\partial U}{\partial \xi} \mid_{\xi=1} - \frac{\partial W}{\partial y} \mid_{y=1} - \frac{\partial W}{\partial y} \mid_{y=0} = 0$$ (1.5)

$$\frac{\partial U}{\partial \xi} \mid_{\xi=0} = 0$$ (1.6)

$$\frac{\partial W}{\partial y} \mid_{y=0} = 0$$ (1.7)

Adsorption experiments showed that the mass of the adsorbate in the gas phase was always below 1% of the sorbed mass, thus $\epsilon_a \text{pr} R$ and $\epsilon_{a,p} \text{pr} R$ are small and can be neglected. With these approximations and eq 1.1, eqs 1.2 and 1.3 can be further simplified to

$$S_a \text{H}_a n_a C_a n_a^{-1} \frac{\partial C_a}{\partial t} = D_a \frac{\partial^2 C_a}{\partial r^2}$$ (1.8)

We can avoid the use of the macro- and micropore-specific surface areas by expressing $S_a \text{H}_a = (1 - \epsilon_a)K_a$ and $S_{a,p} \text{H}_{a,p} = (1 - \epsilon_{a,p})K_{a,p}$ (see Table 1 and Notations) on the left-hand sides of eqs 1 and 2. The equations can be expressed in terms of dimensionless variables $\beta$, $\gamma$, $\delta$, and $\theta$ leading to two dimensionless groups, $\alpha$ and $\beta$ (Table 1 and Notations).

The transformations $U(x,0) = xc(x,0)$ and $W(x,y,0) = yc(x,y,0)$ convert the spherical operator into a rectangular operator (Table 1). The 13 parameters in the original governing differential equations are thus reduced to four: $\alpha$, $\beta$, $\gamma$, and $\delta$. The mathematical problem is to solve two coupled nonlinear diffusion equations (eqs 1.10 and 1.11) with concentration-dependent coefficients, ($U(x,y)$ and $W(x,y)$), which act mathematically as diffusivities. When $n_a = n_i = 1$, the isotherms are linear and the governing equations reduce to those of Ruckenstein et al. (18).

The Freundlich exponents are responsible for the asymmetry in adsorption and desorption curves (32). For values of $n_a < 1$ and $n_i < 1$, the highest asymmetry is observed. When $n_a = n_i = 1$ (the linear case), the desorption curve is a mirror image of the adsorption curve.

The dimensionless group $\alpha$ is the ratio of the time scales of the processes in the macropore- and micropores. The dimensionless group ($\beta; 3a \alpha/n_a n_i$) is the ratio of the micro- and macropore uptake at equilibrium. For the limiting case of ($\beta; 3a \alpha/n_a n_i$) and $\alpha$ approaching zero, the nonlinear Ruckenstein model and similarly the other two biporous models reduce to the homogeneous-pore diffusion model (i.e., one-equation model). The apparent diffusivities, $D_{a,applic}$ and $D_{a,applic}$ (as used in $\alpha$ and $\beta$; see Notations), which account for the retardation of the effective diffusivities due to sorption, are defined at the equilibrium gas-phase concentration, $C_a$ and $C_i$. Thus, the apparent diffusivities expressed in this form are constant values, i.e., independent of concentration.

Equilibrium adsorption experiments usually measure the aggregate (combined macropore and micropore) partition coefficient. Experimental adsorption data are expressed for linear adsorption as the volume-average of the total mass adsorbed per solid volume divided by the gas-phase concentration, the latter expressed as mass adsorbed/void volume. The Freundlich partition coefficient can be expressed as $K = (C_a/\gamma)/(C_n) = (C_i/\gamma)/(C_n)$ since $C_a$ is constant. For a biporous sorbent, the contribution of the sorption equilibrium constants for the macro pores ($K_a$) and micropores ($K_{a,p}$) to the overall partition coefficient ($K$) using the local equilibrium approximation can be expressed for Freundlich adsorption as...
\[
K = K_a + K_i = (\frac{C_{s_a}}{C_{a,0}^n}) + (\frac{C_{s_i}}{C_{i,0}^n}) = (\frac{C_{s_a}}{C_{a,0}^n}) + (\frac{C_{s_i}}{C_{i,0}^n}) = \frac{C_{s_a}}{C_{a,0}^n} + \frac{C_{s_i}}{C_{i,0}^n} (3)
\]

Equation 3 reduces to the linear result when \( n_a = n_i = 1 \). In this study, volume-average quantities, \( \langle X \rangle \) and \( \langle \dot{X} \rangle \), are defined as:

\[
\langle X \rangle = \left(3/R^n \right)^{\frac{1}{n}} X_{r}^2 d_{r} a_{r}
\]

\[
\langle \dot{X} \rangle = \left(9/R^n R^2 \right)^{\frac{1}{n}} X_{r}^2 d_{r} a_{r}
\]

Apart from the method of the present paper, there is no obvious procedure to estimate either the exponents or the partition coefficients for Freundlich isotherms for macropore and micropore zones for a biporous sorbent. For a sorbent composed of aggregated microparticles, this would involve, in practice, discriminating between the adsorption capacity of the outer and inner grain surfaces. Adsorption equilibrium studies usually allow the determination only of the overall coefficients, \( K \), and \( n \). In this work, we will show that under certain conditions \( n_a, n_i, K_a, \) and \( K_i \) can be approximated from the adsorption experiments.

The analytical solution for the microspheres-in-macrosphere model with linear kinetics \( (n_a = n_i = 1) \) can be found in ref 18. For Freundlich adsorption the fractional uptake at any time is

\[
M_t = \frac{\epsilon_a(C_a) + (1-\epsilon_a)K_a(C_a)^n}{\epsilon_a(C_a) + (1-\epsilon_a)K_a(C_a)^n} + \frac{\beta n_i}{3\epsilon_i} \frac{\epsilon_i(C_i) + (1-\epsilon_i)K_i(C_i)^n}{\epsilon_i(C_i) + (1-\epsilon_i)K_i(C_i)^n}
\]

(4)

We developed numerical solutions for all models with implicit (Crank–Nicolson) methods and compared them to explicit numerical schemes. The nonlinear solution to the microspheres-in-macrosphere model was tested by comparing with the analytical solution (18) for the case \( n_a = n_i = 1 \).

Materials and Methods

Yolo silt loam and Na-montmorillonite were adopted as the soil models for this study. Yolo silt loam was obtained from a field location on the University of California, Davis, campus, dried in a greenhouse for 2 days, and then ground to <2-mm particle diameter. The resulting soil was sieved to particle sizes in the range of 500–589 \( \mu m \). Relevant physical characteristics are 1.05% SOM, 33% sand, 49% silt, 18% clay, 0.48 porosity, and 80.6 m\(^2\)/g surface area. Na-montmorillonite (Crook County, WY) was obtained from the Source of Clay Minerals Repository of the University of Missouri–Columbia. Sieved particle sizes in the range of 45–53 \( \mu m \) were collected and oven dried. Relevant physical characteristics are 0.01% SOM, 0.20 porosity, and 83 m\(^2\)/g surface area. Toluene (Fisher, 99.8% pure) was chosen as the VOC.

Experimental Apparatus. Sorption kinetics studies were conducted in the apparatus described by Shonnard et al. (5). The equipment consists of a Cahn RG 2000 electrobalance inside a glass vacuum jar for measurement of the weight change due to sorption. In-line vacuum pumps evacuate the vacuum chamber before the start of the experiment. The temperature of the vacuum chamber in the vicinity of the sorbent sample is obtained with a thermister and a temperature controller. Two separate reservoirs for liquid VOC sources allow toluene vapor to be generated by evaporation.

Experimental Procedure. Before an adsorption experiment was performed, a 300-mg sample in an open glass bottle was outgased in a vacuum oven at 110 °C for at least 12 h. Once the sample was placed in the electrobalance pan it was again desorbed in situ by subjecting the sample to \( \sim 10^{-3} \) Torr vacuum at 110 °C until constant weight was attained. Before opening the VOC reservoir, the sample was allowed to cool to room temperature. The experiment was initiated by opening the VOC source quickly and smoothly until the desired pressure was indicated. The time required to reach the desired pressure was less than 7 s. Small adjustments to maintain constant pressure were made as needed by briefly opening the VOC reservoir valve. The kinetics experiments were run at relatively low vapor concentrations, 0.16 \( < P/P^0 < 0.18 \), to minimize adsorption temperature effects. Blanks were run for several days to monitor buoyancy and the instability of the electrobalance; these effects were negligible. The use of a well-characterized system, such as single-component vapor diffusion into soil particles in a low pressure environment, provides the simplest framework to study the adsorption and diffusion mechanisms in soil particles. This experimental approach avoids dispersion, convection, and mixing that might cloud the actual transport mechanisms when column or batch methods are used.

Equilibrium Sorption Experiments. To determine equilibrium isotherms, which can take days to weeks for each equilibrium point, the electrobalance was not a convenient device. Equilibrium partitioning in closed systems (EPICS) (33–35) with headspace gas chromatography was more appropriate since several equilibrium points can be determined simultaneously in separate vessels. The technique was refined by (i) allowing enough time to achieve adsorption equilibrium, i.e., more than 2 weeks, as previously determined for several points with the electrobalance (only a few hours to a few days were allowed in most previous studies); (ii) using moisture-free soil samples; and (iii) using a sterilizing agent to avoid VOC biodegradation (1000 ppm by weight of HgCl\(_2\)). Several equilibrium points were also collected with the electrobalance to confirm the results obtained with the EPICS technique.

The refined EPICS method to construct toluene vapor sorption isotherms is a material balance procedure involving accurate measurement of the headspace concentration of spiked samples in closed vessels by gas chromatography. Open amber glass bottles with and without soil samples were outgassed at 150 °C in a small vacuum oven for at least 12 h. Preliminary experiments with the microlance revealed that only a few seconds were sufficient for readsorption of moisture from the air. Moisture is a strong competitor for adsorption sites and must be eliminated to avoid adsorption interference. To avoid water vapor readsorption while opening the vacuum oven, the glass bottles placed at the bottom of the oven chamber were surrounded by abundant CaSO\(_4\) desiccant (additional desiccant was located at the small oven entrance). After the outgasing period, samples under vacuum were allowed to cool to room temperature. To open the oven, the vacuum was released, and the bottles were abundantly flushed with a large helium stream and quickly capped in situ. The amber glass vials (42-mL Qorpak, Fisher Scientific) were
capped with septum-featured Teflon valves (Mininert, Dynatech). Various amounts of liquid toluene (1–150 µL) were added to bottles loaded with up to 7 g of sorbent using a Gastight microsyringe. Toluene spiking levels were further verified by weighing the bottles before and after toluene addition. Bottles fixed to a rotating vertical wheel were tumbled end-over-end at 1 rpm for at least 2 weeks. Headspace vapors were withdrawn with a Gastight microsyringe and analyzed by direct injection into a gas chromatograph (8500 Series Perkin Elmer) equipped with crosyringe and analyzed by direct injection into a gas Heedspace vapors were further verified by weighing the bottles before and after toluene addition. Bottles fixed to a rotating vertical wheel were tumbled end-over-end at 1 rpm for at least 2 weeks. Headspace vapors were withdrawn with a Gastight microsyringe and analyzed by direct injection into a gas chromatograph (8500 Series Perkin Elmer) equipped with a 30 m × 0.52 mm Megaboard column (DB-624, J & W Scientific) and a flame ionization detector (GC-FID). Control samples with various amounts of toluene and with no sorbent were run to account for toluene sorption to vial walls and to construct a GC–response calibration curve.

## Results and Discussion

### Sorption Equilibrium

Figure 2 shows the total (macropore plus micropore) equilibrium uptake obtained using the EPICS method for Yolo silt loam and Na-montmorillonite. Results agreed within 5% with the equilibrium points obtained by the gravimetric method. This indicates that the two methods are complementary for equilibrium and kinetics studies, specifically for the slow adsorption–diffusion behavior observed here. Freundlich isotherms were fitted to the data (Figure 2) and are given in Table 2.

![Figure 2](image)

FIGURE 2. Toluene equilibrium isotherms for (A) Yolo silt loam and (B) Na-montmorillonite. Solid lines represent Freundlich fits, and dashed lines represent BET fits. The points (+) for total uptake were measured by the electrobalance method. Values of the isotherm parameters are given in Table 2.

## Summary of Toluene Vapor-Phase Freundlich Equilibrium Isotherms and Sorption Kinetics

<table>
<thead>
<tr>
<th></th>
<th>Yolo silt loam</th>
<th>Na-montmorillonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_e$ (cm)</td>
<td>$2.72 \times 10^{-2}$</td>
<td>$2.45 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\epsilon_o$</td>
<td>0.22</td>
<td>0.09</td>
</tr>
<tr>
<td>$\epsilon_i$</td>
<td>0.26</td>
<td>0.11</td>
</tr>
<tr>
<td>$n_o$</td>
<td>0.397</td>
<td>0.696</td>
</tr>
<tr>
<td>$n_i$</td>
<td>0.427</td>
<td>0.568</td>
</tr>
<tr>
<td>$\beta$ (mg/g)</td>
<td>38.2</td>
<td>50.2</td>
</tr>
<tr>
<td>$K_i$ (mg/g)</td>
<td>41.3</td>
<td>42.7</td>
</tr>
<tr>
<td>$K_o$ (mg/g)</td>
<td>78.7</td>
<td>92.4</td>
</tr>
<tr>
<td>$P$ (torr)</td>
<td>4.5</td>
<td>5.0</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$2.5 \times 10^{-5}$</td>
<td>$6.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\beta_n/3\alpha_n$</td>
<td>1.4</td>
<td>1.1</td>
</tr>
<tr>
<td>$D_{app}/R_o^2$ (1/s)</td>
<td>$2.0 \times 10^{-2}$</td>
<td>$1.6 \times 10^{-2}$</td>
</tr>
<tr>
<td>$D_{app}/R_i^2$ (1/s)</td>
<td>$4.8 \times 10^{-7}$</td>
<td>$1.1 \times 10^{-9}$</td>
</tr>
<tr>
<td>$D_{app}$ (cm²/s)</td>
<td>$1.5 \times 10^{-5}$</td>
<td>$9.7 \times 10^{-8}$</td>
</tr>
<tr>
<td>$D_{app}$ (cm³/s)</td>
<td>$0.48 \times 10^{-14}$</td>
<td>$1.1 \times 10^{-14}$</td>
</tr>
<tr>
<td>$D_{eff}$ (cm²/s)</td>
<td>$3.8 \times 10^{-3}$</td>
<td>$3.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>$D_{eff}$ (cm³/s)</td>
<td>$1.2 \times 10^{-12}$</td>
<td>$3.7 \times 10^{-12}$</td>
</tr>
<tr>
<td>COD</td>
<td>0.998</td>
<td>0.993</td>
</tr>
</tbody>
</table>

*The isotherms are for macropores, $C_m = K_m(P/P_o)^n_i$; micropores, $C_m = K_m(P/P_o)^n_a$; and total (macropores plus micropores), $C_m = K_m(P/P_o)^n_i^n_a$.

*Assuming $R_i = 1 \mu$m. *COD = 1.0 for a perfect fit.

![Figure 3](image)

FIGURE 3. Comparison of the experimental history curve for adsorption of toluene on Na-montmorillonite with the nonlinear homogeneous-pore model and several values of apparent diffusivity (cm²/s).

The BET isotherm was also fitted to the equilibrium data without improvement in the range of $0 < P/P_o < 0.6$. To describe the dynamic behavior of soil sorption, specifically in the range of relative partial pressure used in this work ($P/P_o < 0.18$), the Freundlich isotherm served adequately.

Sorption of toluene on Yolo silt loam and on Na-montmorillonite occurred in two stages, readily distinguished in the semilog plots of Figures 3 and 4. The adsorption and diffusion in macropores rapidly reached a (partial) equilibrium point in the first stage of the process, followed by a slow approach to (total) adsorption equilibrium in micropores. This two-stage adsorption (or desorption) on soil has been observed previously (9, 15).

The adsorption uptake vs log of time shows a distinct knee marking the neighborhood of the total macropore adsorption capacity (Figure 4). Since micropore uptake...
rate was several orders of magnitude slower than the macropore rate, the micropore contribution to the (total) mass uptake before this knee point can be considered negligible. This allows one to isolate macropore and micropore adsorption capacities and to measure macropore and micropore equilibrium isotherms independently. The microbalance method was appropriate to measure the equilibrium macropore uptake since this occurred in the first few minutes of an adsorption experiment. For the macropore sorption equilibrium experiments, the pressure of the electrobalance chamber was set to the desired partial pressure by opening the VOC reservoir and allowing the sample to adsorb until the appearance of the curve knee. When the adsorption rate abruptly slowed, the system was ready for the next point, and the pressure was then increased to obtain a new macropore equilibrium point. The macropore and total equilibrium uptake isotherms independently. The micropore adsorption capacities and to measure macropores and micropore equilibrium isotherms in Figure 2 and Table 2.

As shown in Table 2, the values of the Freundlich exponent determined by least-squares fitting for macropores and micropores agreed within 20%, indicating that the surfaces exhibit similar adsorption behavior. The micropore uptake was obtained by subtracting the macropore uptake from the total uptake. The differences in the equilibrium constant for micropore and macropore (inner and outer particle) surfaces indicate differences in the available surface area for adsorption.

Homogeneous-Pore Diffusion Model. The homogeneous-pore model is appropriate for diffusion in pores of fairly uniform size (3, 9, 14). In the current work, this model failed to represent the adsorption history curve, confirming that more than one diffusional mechanism was involved. As shown in Figure 3, this model does not properly account for transport when two diffusion processes with distinct time scales are involved.

Microspheres-in-Macrosphere. This model describes the toluene adsorption history quite well as shown in Figure 4. The evaluation of the transport parameters entailed curve fitting the experimental data by trial and error. Error analyses were carried out between the experimental and calculated data for each model. The coefficient of determination, COD or R², as defined in Notations, is a measure of the goodness of fit. Values of COD in Table 2 are close to unity, indicating good agreement between model calculations and experimental data.

Considering that the clay fraction has the largest adsorption capacity, we assume the micropore radius, \( R_i \), to be 1 \( \mu m \) (31) to calculate \( D_{app} \). Pignatello et al. (15) measured the uptake in each soil fraction and suggested that the diffusive medium in soils consists of \( \leq 2 \mu m \) diameter microparticles. To calculate the effective diffusivities from the fitted apparent diffusivities, the values of the average porosities \( (\epsilon_a \ and \ \epsilon_i) \) were estimated by the method of Emmett and Brunauer (36) as described by Smith (37). We assumed, following Wakao and Smith (38), that the area fractions are the same as the volume void fractions.

Our values for the effective diffusivities in the micropore zone (10⁻¹² cm²/s) (Table 2) are in accord with literature values for adsorption and diffusion in zeolites (10⁻²³, 10⁻¹² cm²/s) (13) and ion exchange resins (10⁻¹⁹–10⁻¹² cm²/s) (18). The values for the effective diffusivities in the macropore zone for both systems (10⁻⁶–10⁻³ cm²/s) agree with values reported in the literature for other soil systems (3–5). If \( R_i \) for the diffusive medium is assumed smaller than 1 \( \mu m \), the resulting micropore diffusivity will be even smaller. We neglect transfer resistance at the outer surface of the microparticles for the Ruckenstein model and at the micropore mouth for the in-series cylindrical networks model. The extremely large Biot number (\( Bi = D_{app}/D_{eff} \sim 10^3 \)) calculated at the interface justifies this procedure.

Equilibrium and kinetics experiments revealed that ~42% for Yolo silt loam and ~48% for montmorillonite of the toluene mass adsorbed at macropores. This confirmed that the outer microsphere surfaces (macropore surfaces) play an important role in soil adsorption.

Macrosphere with In-Series Cylindrical Macropore and Micropore Networks. In Figure 1D, micropores and macropores are idealized as in-series cylindrical tubes encased in a macrosphere. Cylindrical micropores are considered open to the macropore and closed at the opposite end. This geometrical configuration for the macropore–micropore structure was originally proposed by Turner (24) and evaluated for linear adsorption by Peterson (23). As in the Ruckenstein model, two dimensionless groups characterize the nonlinear adsorption model with corresponding physical meaning. Numerical simulations with this model produced values for macropore effective diffusivities similar to the Ruckenstein model. The micropore effective diffusivities, based on a characteristic micropore length of 1 \( \mu m \) (i.e., equal to the assumed microsphere characteristic radius in the Ruckenstein model), were of the same order of magnitude as the Ruckenstein model but three times higher. Slightly better
fittings were obtained with the Ruckenstein model than with this model.

**Macro pore with Independent Micropore and Macropore Networks.** In this simplification, Figure 1B, micropores and macropores are considered as two independent networks, sharing the same adsorbent body but with no internal connections. This model is physically equivalent to considering the pore medium as an assemblage of porous spheres of the same diameter with different average pore sizes. This model considers the diffusion in macropores in parallel with the diffusion into micropores. Effective diffusivities in the micropores ($10^{-9}$–$10^{-8}$ cm$^2$/s) were larger than with the microspheres-in-macrosphere model ($10^{-12}$ cm$^2$/s), which considers the diffusional contribution of both networks in series. The characteristic diffusion distance for both micropores and macropores is the macrosphere radius, i.e., $R = R_s$ ($2.72 \times 10^{-2}$ cm for Yolo and $2.45 \times 10^{-3}$ cm for montmorillonite). To achieve a reasonable value of micropore diffusivity, it would be necessary to assume that the length scale for micropore diffusion is $R_s = 1 \mu$m, as for the microspheres-in-macrosphere model. Micropore diffusivities would then agree within 6% of the results obtained with the Ruckenstein model. Although this model can quantitatively describe adsorption rates, it is an unrealistic pore structure model for adsorbents made of aggregated particles.

**Conclusion**

The biporous models can thus describe reasonably well the adsorption history of toluene in Yolo soil and montmorillonite. Discrimination between the models should be based on the internal network structure of the soil agglomerates, which at present is not well understood.

Most research on adsorption is for experiments of short duration, but recent investigations reveal that adsorption and desorption in soils occur over longer time scales (9, 14, 15, 39–41). If adsorption equilibrium is not achieved, the calculated value of the diffusivity will depend on the duration of the pseudoequilibrium experiment. For instance, the ratio of micropore uptake to macropore uptake ($\beta = 4 \times 3 \mu$m) will increase for longer pseudoequilibrium adsorption experiments due to the slow increase in micropore adsorption capacity. Similarly, increasing the time span for micropore penetration in a pseudoequilibrium experiment will decrease the ratio of the time scales for mass penetration in macropores and micropores, $\alpha$. Similar problems are expected for desorption experiments started from nonequilibrium states. The slow diffusion and adsorption in the soil micropores have not been widely recognized in previous soil adsorption studies. A slow approach to equilibrium in several experimental techniques is difficult to notice due to analytical limitations. This limitation is overcome with the gravimetrical electrobalance method where weight changes of $10^{-7}$ g can easily be detected. As pseudoequilibrium experiments will in general predict larger diffusivities, achieving true equilibrium is essential for accurate measurement of diffusivities.

In the current research, guided by previous work on soil adsorption, we used a relatively large aromatic molecule (toluene) at concentrations $0.16 < C_{bulk} < 0.18$. Na-montmorillonite with low SOM content ($<0.01\%$) and Yolo silt loam with moderate SOM content ($<1.0\%$) were chosen as sorbents. The small contribution to sorption of the SOM content in Yolo silt loam is lumped into the macropore and micropore sorption capacities in the present work. Na-montmorillonite SOM content is negligible. This work and several others (9, 15, 39, 40) suggest that mineral surfaces play a major role in VOC adsorption.

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**Notations**

- $C_a$ macropore gas-phase concentration, mg/cm$^3$ gas
- $C_{a0}$ macropore gas-phase concentration at zero time, mg/cm$^3$ gas
- $C_{a\infty}$ macropore gas-phase concentration at equilibrium, mg/cm$^3$ gas
- $C_a/(C_a - C_{a\infty})$, gas-phase macropore dimensionless concentration
- $C_{bulk}$ outside macrosphere (bulk) concentration, mg/cm$^3$ gas
- $C_{bulk}^\sigma$ saturated bulk concentration, mg/cm$^3$ gas
- $C_i$ micropore gas-phase concentration, mg/cm$^3$ gas
- $C_{i0}$ micropore gas-phase concentration at zero time, mg/cm$^3$ gas
- $C_{i\infty}$ micropore gas-phase concentration at equilibrium, mg/cm$^3$ gas
- $C_{i,p}/(1 + \epsilon_i^p)$, micropore sorbed concentration, mg/cm$^3$ solid
- $C_{i,p}(1 - \epsilon_i^p)$, micropore sorbed concentration, mg/cm$^3$ solid
- $C_m$ gas-phase concentration at equilibrium, mg/cm$^3$ macrosphere
- $D_a$ macropore diffusivity, cm$^2$/s
- $D_{a,app}$ $D_{a,app}/(S_i H_i n_i C_m^{n_i - 1})$, macropore apparent diffusivity, cm$^2$/s
- $D_{a,app}/C_m$, $D_{a,app}/(S_i H_i n_i C_m^{n_i - 1})$, macropore apparent diffusivity evaluated at $C_m$, cm$^2$/s
- $D_i$ micropore diffusivity, cm$^2$/s
- $D_{i,eff}$ micropore effective diffusivity, cm$^2$/s

- $\tilde{\rho}$ micropore gas-phase concentration, mg/cm$^2$
- $\tilde{\epsilon}_i^p$, micropore sorbed concentration, mg/cm$^3$ solid
- $\tilde{\epsilon}_i$, micropore effective diffusivity, cm$^2$/s

- $\tilde{\rho}$ micropore gas-phase concentration, mg/cm$^2$
- $\tilde{\epsilon}_i^p$, micropore sorbed concentration, mg/cm$^3$ solid
- $\tilde{\epsilon}_i$, micropore effective diffusivity, cm$^2$/s

- $\epsilon_i^p$, micropore sorbed concentration, mg/cm$^3$ solid
- $\epsilon_i$, micropore effective diffusivity, cm$^2$/s

- $\epsilon_i$, micropore effective diffusivity, cm$^2$/s

- $\epsilon_i$, micropore effective diffusivity, cm$^2$/s
\( D_{\text{app}} \) - micropore apparent diffusivity, cm\(^2\)/s
\( D_{\text{app}}/C_m \) - micropore apparent diffusivity evaluated at \( C_m \), cm\(^2\)/s
\( H_a \) - radial coordinate, cm
\( P \) - partial pressure, torr
\( P_r \) - relative partial pressure, dimensionless
\( \tau_i \) - time, s
\( X_{C_p} \) - dimensionless variable
\( \epsilon \) - overall average porosity, cm\(^3\) pore/cm\(^3\) macropore
\( \epsilon_a \) - macropore average porosity, cm\(^3\) pore/cm\(^3\) macropore
\( \epsilon_i \) - micropore average porosity, cm\(^3\) pore/cm\(^3\) macropore
\( \epsilon_{i,p} \) - microsphere average porosity, cm\(^3\) pore/cm\(^3\) microsphere
\( \eta \) - (1 - \( \epsilon_a \))/(4/3)\( r_i^3 \) (volume of microparticles/unit macropore volume)/unit microsphere volume (i.e., number of micropores per macropore)

**Literature Cited**


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