Effect of Solute Concentration on Sorption of Polyaromatic Hydrocarbons in Soil: Uptake Rates

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The effect of solute concentration on sorption kinetics may be a factor in determining bioavailability and transport of organic pollutants in soils and sediments, but there is conflict in the literature over whether sorption is concentration-dependent. Sorption of phenanthrene and pyrene to seven soils ranging in organic carbon (OC) content from 0.18 to 43.9% was studied. Careful analysis revealed that experimentally the normalized rate of approach to equilibrium for compounds exhibiting a concave-down (with respect to the solute concentration axis) nonlinear isotherm increases with concentration. However, the effect is rather small and is most apparent when the fraction of total solute finally taken up by the solid (F) is low. The explanation is rooted in the nonlinearity of the isotherm and the finite-bath condition of the experiment and can be expressed in terms of two opposing effects. On the one hand, the apparent diffusivity of a (concave-down) nonlinearly sorbing compound within particles increases with concentration because its affinity for the solid phase decreases with increasing concentration. On the other hand, rates in finite-bath reactors carried out at the same liquid/solid ratio will suffer from a batch process temporal bias called the “shrinking gradient” effect. It is an artifact of the methodology and is due to gradient driving forces that slow the sorption rate as F declines. In nonlinear cases F declines as concentration increases. The shrinking gradient effect vanishes as the liquid/solid ratio approaches infinity. Although this effect is self-correcting when an appropriate nonlinear diffusion model is applied, consensus about such models has not yet been achieved. To provide bounds for the shrinking gradient effect in finite-bath systems semiempirically, two models that give lower and upper bounds of the characteristic sorption time r in the limit of infinite bath have been employed: (a) a wetting front model, which assumes sorption is rate-limited by molecular migration, and (b) a fast diffusion model, which assumes a mass-transfer resistance at the sorption site. The results are consistent with an intrinsic positive concentration dependence of sorption kinetics.

Introduction

The rates of sorption and desorption often control the physical availability and biological activity of organic pollutants in geosorbents (1–3). The physical structure of soil or sediment organic matter (SOM) plays an important, if not dominant, role in governing sorption kinetics, because the SOM fraction ordinarily exerts the greatest thermodynamic affinity for hydrophobic compounds. Recent studies have demonstrated the heterogeneous sorption potential of SOM toward hydrophobic compounds in many geosorbents, and several explanations have been advanced for its cause (4–15). Isotherms are typically nonlinear “concave down” with respect to the solute concentration axis; that is, they show weakening affinity of the sorbate for sorbent with increasing loading. When molecular diffusion within the sorbent is rate-controlling, nonlinear systems are predicted to show a concentration-dependent apparent diffusion coefficient. For concave-down isotherms the affinity of the solid phase for the sorbate molecule decreases with increasing concentration. Because the driving force for diffusion is the gradient in chemical potential, the apparent diffusion coefficient should increase with concentration in such cases (16). This follows from the Stefan–Maxwell formalism for diffusion (16), in which the apparent diffusivity (D_a) is related to the self-diffusivity (D_0) and a thermodynamic correction factor d ln C/d ln q (C is the solute concentration and q the sorbed concentration) that arises from the nonlinearity of the relationship between activity and concentration in the solid phase:

\[ D_a = D_0 (d \ln C/d \ln q) \]  

(1)

When the isotherm is linear, D_a = D_0. Although predicted by theory and inferred in a number of experiments, the direct demonstration of concentration-dependent kinetics with respect to geosolids is ambiguous and has even been outright challenged. A number of studies have shown that when the Freundlich equation

\[ q_{eq} = K_F C_{eq}^{1/n} \]  

(2)

(where q_{eq} and C_{eq} are equilibrium sorbed [\mu g/g] and dissolved [\mu g/mL] concentrations and K_F and N are constants) is used to fit intermediate-time sorption data, the Freundlich exponent N decreases with time (9, 12, 17). This suggests an accelerating approach to equilibrium with increasing concentration, because log (q_{eq}/q_{final}) at constant C increases progressively along the solute concentration axis. Graber and Borisover (10, 18–20) have claimed that the Freundlich equation is inappropriate for describing intermediate-time sorption data. After analyzing published normalized uptake data, they called into question any effect of concentration on normalized rate of approach to equilibrium. Huang and Weber (12) maintained that quicker attainment of equilibrium is reached at a higher, rather than a lower, concentration of phenanthrene in several natural solids. However, an inspection of their data (Table 1 and Figures 3 and 4 of ref 12) reveals mixed results: about half of the solids appeared to show faster attainment of equilibrium at higher concentrations, whereas the other half showed the opposite result or were inconclusive because sorption was continuing at a significant pace at both concentrations. In any case, whether approach to equilibrium was more rapid in one case or the other was not evaluated quantitatively. Schlebaum et al. (21) proposed faster attainment of equilibrium at a higher concentration of pentachlorobenzene on the basis of a demonstrable “aging” effect; that is, slower desorption with increased precontact time, at a lower concentration that was absent at the higher concentration. Although this is consistent with...
with the postulate, the aging effect was rather small and applied to only one soil; thus, it amounts to weak and decidedly indirect evidence of a general concentration effect on kinetics. Other studies have found that formation of a fraction that is highly resistant to desorption is greater at lower than at higher sorbate loading (1), but such findings address the issue in an oblique way, at best.

In this paper we attempted to address the issue of concentration-dependent sorption kinetics systematically by examining phenanthrene and pyrene uptake rates in various soils ranging in organic carbon (OC) content from 0.18 to 43.9%. Our approach was twofold. The first set of experiments employed a mathematical criterion to determine which of two greatly different initial solute concentrations first approached "equilibrium" in mixed batch reactors. A second set of experiments established directly the concentration dependence of the characteristic sorption time, \( t_r \), an indicator of the time needed for the bulk of contaminant to attain sorptive equilibrium.

We find that the approach to equilibrium is indeed concentration-dependent as predicted by theory but that the mixed and conflicting results in the literature are probably due to an opposing effect mostly overlooked until now. The opposing effect applies to nonlinearly sorbing compounds and is an artifact of the methodology commonly used for solution-solid systems—that of conducting the experiment in a finite bath. The finite bath is convenient because it allows sorption to be monitored by measuring the decrease in aqueous phase concentration over time. The experimental procedure itself, however, changes the temporal behavior of the sorption process due to the decreasing ambient aqueous concentration. For diffusion processes it is common knowledge that, due to the gradient driving force, the fractional rate of uptake \( \frac{dQ}{dt} \), where \( Q = q(t)/q_{\text{eq}} \), decreases as the fraction, \( F \), of total solute added finally taken up by the solid declines from values close to 1 at low liquid/solid ratios to 0 in an infinite bath (22). If the same liquid/solid ratio is used over the whole range of concentrations tested of a compound that sorbs in a concave-down nonlinear fashion, \( F \) will decrease with increasing concentration due to the nonlinearity, subjecting observed rates to a "shrinking gradient" effect.

A mechanistic kinetic model that incorporates nonlinearity should automatically correct for the shrinking gradient effect. We have proposed a nonlinear sorption kinetic model for SOM that correctly predicts the concentration dependence of sorption (23). At the present time, however, the mechanisms of sorption are debatable, and selection of a mathematical diffusion model cannot be made with complete confidence. Ball and Roberts (24) recognized the effect of \( F \) on \( q_{\text{eq}} \), and, second, because the distribution coefficient is a function of \( C \) and, second, because the apparent diffusivity is expected to be concentration-dependent. In this paper we use two semiempirical models to provide upper and lower bounds for the shrinking gradient effect and thus provide an estimate of the lower and upper bounds of the sorption characteristic time \( t_r \) for the limiting infinite-bath case. In a forthcoming paper we will address the issue of concentration-dependent desorption.

**Experimental Section**

**Materials.** The soils and their OC contents (dry weight basis) are as follows: Cheshire fine sandy loam (1.4% OC), Pahokee (43.9% OC), Wurtsmith AFB 1AB (0.18% OC), Mount Pleasant silt loam (4.45% OC), Port Hueneme (0.62% OC), Seal Beach (1.48% OC), and modified Seal Beach (0.74% OC). Wurtsmith AFB 1AB was provided by Michael Barcelona (National Center of Integrated Bioremediation Research and Development, University of Michigan, Ann Arbor, MI). Ernest Lory of the National Test Site Program, Port Hueneme, provided Port Hueneme and Seal Beach soils. Seal Beach soil was reported to be contaminated with up to 3600 mg/kg of Bunker C oil (private communication, National Test Site Program, Port Hueneme, CA). To address the potential effects of this oil on the uptake of phenanthrene, a modified Seal Beach soil sample was prepared by extracting Seal Beach soil with pentane (Aldrich, 99%). The modified soil was then dried at 40°C for 3 h under vacuum. Additional properties of Cheshire, Mount Pleasant, and Pahokee soils are given elsewhere (5, 25–27). The Pahokee soil was received dry and passed through a 0.5-mm sieve. The others were air-dried and passed through a 2-mm sieve. All soils were sterilized with 2.5 M rads of Co-60 radiation from a Co-60 source (Ward Laboratories, Cornell University, Ithaca, NY). [1,10,13-C]Phenanthrene (> 98%, 46.9 mCi/mmol) and [4,5,9,10-14C]Pyrene (> 98%, 58.7 mCi/mmol) and their unlabeled forms were purchased from Sigma Chemical Co. (St. Louis, MO). Because results here relate to ongoing biodegradation studies, the aqueous phase for all
experiments was an inorganic salts solution at pH 7.1 (25) containing NaN₃ (0.2 g/L) to inhibit bacterial growth.

**General Procedures.** To ensure that a random particle size distribution was delivered to individual replicate bottles, soils were homogenized in a moistened state (10–45% distilled water) prior to weighing. Indicated amounts of soil used refer to the oven-dry weight. For each experiment prepared soil suspensions in salts solution received identical amounts of either [¹⁴C]phenanthrene or [¹⁴C]pyrene and enough unlabeled PAH to reach the target concentration. The carrier solvent, methanol, comprised <0.2% of the total liquid volume and was equal in all samples and controls of a given experiment. Sample vessels were mixed end-over-end at 21 °C on Rugged Rotator shakers (Glas Col, Terre Haute, IN) operating at 15 rpm. At timed intervals, the vessels were centrifuged at (depending on the soil) 1350–2200 rpm for 12–20 min at 21 °C. A portion of the supernatant was then removed and the radioactivity measured by liquid scintillation counting in 15 mL of Opti-Fluor (Packard Instrument Co.). As determined by solubility enhancement experiments (25), phenanthrene sorption to nonsettling colloidal OC from Pahokee and Cheshire soils was negligible as long as the total nonpurgeable OC concentration was <30 mg/L. However, pyrene sorption to nonsettling OC was not negligible, so aqueous pyrene concentrations reported here are corrected using $K_{\text{colloids}}$ calculated from the slope of apparent solubility vs nonpurgeable OC (data not shown).

**Sorption Kinetics.** Suspensions of Cheshire soil (0.09 g for phenanthrene, 0.05 g for pyrene) in 160 mL were prepared in 160-mL crimp-cap glass bottles fitted with PTFE-lined inserts. The suspensions were amended with (2.17–2.50) × 10⁵ Bq of radiolabeled PAH and nonlabeled PAH to achieve 154 or 90200 μg of phenanthrene/g of OC and 348 or 20900 μg of pyrene/g of OC. Samples of Pahokee soil (0.013 g for phenanthrene and 0.011 g for pyrene) in 250-mL salts solutions were prepared in 250-mL screw-cap glass bottles fitted with PTFE-lined septa. The suspensions were amended with 128 or 29900 μg of total phenanthrene/g of OC and 214 or 4800 μg of total pyrene/g of OC, including (7.10–10.7) × 10⁵ Bq of radiolabeled forms. At the end of the sorption experiment, samples of Cheshire soil containing phenanthrene or pyrene were extracted with methanol (15–20 mL) for 4 h at 70 °C. The recovery of initially added radioactivity was 100.3 ± 5.3% (pooled data for both soils and both compounds).

A similar procedure was used to develop time-dependent sorption curves for the estimation of characteristic sorption times. Samples of Wurtsmith AFB 1AB (0.7 g and 40 mL), Mount Pleasant (0.06 g and 55 mL), Pahokee (0.018 g and 160 mL), Port Huene me (0.25 g and 55 mL), Seal Beach (0.1 g and 55 mL), modified Seal Beach (0.217 g and 55 mL), and Cheshire soils (0.08 g and 55 mL) were prepared in vials or bottles of appropriate size fitted with Al foil-covered PTFE-lined septa. The suspensions were amended with 128 or 29900 μg of total phenanthrene/g of OC and 214 or 4800 μg of total pyrene/g of OC, including (7.10–10.7) × 10⁵ Bq of radiolabeled forms. At the end of the sorption experiment, samples of Cheshire soil containing phenanthrene or pyrene were extracted with methanol (15–20 mL) for 4 h at 70 °C. The recovery of initially added radioactivity was 100.3 ± 5.3% (pooled data for all seven soils).
### TABLE 2. Effect of PAH Concentration on the Time to Reach Sorption Equilibrium in Seven Soils.

<table>
<thead>
<tr>
<th>Soil</th>
<th>PAH</th>
<th>$C_0^2$ (µg/mL)</th>
<th>$F_{\text{final}}$</th>
<th>Criterion for equilibrium, $dF/dt$ (10⁻⁶/day)</th>
<th>Time to equilibrium (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Part I</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cheshire</td>
<td>phenanthrene</td>
<td>0.00121</td>
<td>0.299</td>
<td>4.10</td>
<td>52</td>
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<tr>
<td></td>
<td>pyrene</td>
<td>0.710</td>
<td>0.119</td>
<td>1.64</td>
<td>17–35</td>
</tr>
<tr>
<td>Pahokee</td>
<td>phenanthrene</td>
<td>0.00292</td>
<td>0.620</td>
<td>8.50</td>
<td>&gt;64</td>
</tr>
<tr>
<td></td>
<td>pyrene</td>
<td>0.0914</td>
<td>0.298</td>
<td>4.08</td>
<td>35–57</td>
</tr>
<tr>
<td><strong>Part II</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pahokee</td>
<td>phenanthrene</td>
<td>0.00243</td>
<td>0.860</td>
<td>11.8</td>
<td>&gt;100</td>
</tr>
<tr>
<td>Mount Pleasant</td>
<td>phenanthrene</td>
<td>0.363</td>
<td>0.601</td>
<td>8.23</td>
<td>60</td>
</tr>
<tr>
<td>Cheshire</td>
<td>phenanthrene</td>
<td>0.112</td>
<td>0.469</td>
<td>6.42</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>phenanthrene</td>
<td>0.635</td>
<td>0.377</td>
<td>5.16</td>
<td>120–180</td>
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<tr>
<td>Wurtsmith AFB 1AB</td>
<td>phenanthrene</td>
<td>0.00966</td>
<td>0.496</td>
<td>6.79</td>
<td>&gt;120</td>
</tr>
<tr>
<td>Port Hueneme</td>
<td>phenanthrene</td>
<td>0.726</td>
<td>0.240</td>
<td>3.29</td>
<td>38–64</td>
</tr>
<tr>
<td>modified Seal Beach</td>
<td>phenanthrene</td>
<td>0.00497</td>
<td>0.679</td>
<td>9.30</td>
<td>121–180</td>
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<tr>
<td>Seal Beach</td>
<td>phenanthrene</td>
<td>0.009790</td>
<td>0.672</td>
<td>9.20</td>
<td>121–180</td>
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<tr>
<td></td>
<td></td>
<td>0.998</td>
<td>0.715</td>
<td>9.80</td>
<td>60</td>
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</tbody>
</table>

*Initial solute concentration for uptake experiments. ¹ Equilibrium is arbitrarily defined as a rate of fractional uptake ($dF/dt$) of $1.5 \times 10⁻⁶$, equivalent to a 1% increase in the fraction sorbed within 2 years.

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### Results

**Uptake Rates: Rate of Approach to Equilibrium.** The first set of experiments established which of two greatly different initial PAH concentrations in the Cheshire and Pahokee soils approached sorptive equilibrium more rapidly. Because equilibrium means zero net rate, and zero net rate is difficult to establish in practice, we arbitrarily define equilibrium to be a rate $\leq 0.5\%$ per year increase in the ratio $F$, mass sorbed to the total mass added. Plots of $F$ vs time were generated. Two of the four graphs, chosen at random, are illustrated in Figure 1: uptake of 0.710 and 0.00121 µg/mL initial phenanthrene concentrations by Cheshire soil and uptake of 0.0927 and 0.0043 µg/mL initial pyrene concentrations by Pahokee soil. Note that the graphs have separate ordinates for each concentration and that the scale is adjusted so that points for the final $F$ are superimposed.

As expected from the nonlinearity of the isotherms for these two soils (Table 1), the final value of $F$ decreased with increasing initial solute concentration in all cases (Table 2). The form in which the curves in Figure 1 are plotted (superposition of the final $F$ points) gives the impression of slightly faster rates of uptake at the higher concentrations. To quantitatively determine which concentration attained “equilibrium” more quickly, the following approach was used. First, the fractional uptake rate ($dF/dt$) was calculated as the slope of the linear regression line through points from day 6 to the final point taken (84 days for Cheshire or 120 days for Pahokee). The starting point was chosen arbitrarily by taking into consideration the fact that this study focuses on the tailing effect (slow approach to equilibrium) rather than initial rates of uptake. Serial slopes were determined for each curve by moving one sample point closer to the last point and then recalculating the slope of the regressed line. The criterion values of $dF/dt$, which are different for each case because $dF/dt$ is a function of $F$ (22), are given in Table 2, part I, for all cases and shown in Figure 2 for the two representative cases. One can observe that the higher solute concentration always reaches equilibrium more quickly than the lower.

**Uptake Rates: Concentration Dependence of the Characteristic Sorption Time.** A second set of experiments established directly the concentration dependence of the characteristic sorption time $\tau$ for phenanthrene in seven soils. $\tau$ is defined as the mean time for sorptive uptake and is illustrated hypothetically in Figure 3. Figure 4 shows a series of plots of $Q$ for phenanthrene on Port Hueneme soil (Figure 4a) and Pahokee soil (Figure 4b) against the square root of time for several initial dissolved phenanthrene concentrations. As can be seen for these two soils, the lowest initial concentration seems to attain equilibrium more quickly than the higher initial concentrations. However, when the serial slope test described in the previous section was applied to all soils, mixed results were obtained (Table 2, part II). The higher solute concentration reaches equilibrium more quickly than the lower solute concentration in four cases (Pahokee, Cheshire, Seal Beach, and Wurtsmith AFB 1AB); the opposite occurs in two other cases (Port Hueneme and Mount Pleasant), and modified Seal Beach did not show any concentration dependence. The apparent incongruity between experiment and theory may be explained by the opposing effects described in the introduction: in the direction of increasing concentration, the rate of sorption is enhanced by an increase in the intrinsic apparent diffusion coefficient, and the rate is also inhibited by the shrinking gradient effect.

The shrinking gradient effect can be eliminated experimentally either by (a) carrying out sorption under conditions approximating infinite bath or (b) adjusting the solid-to-water ratio at each concentration to achieve the same fraction of total solute finally taken up ($F$). Because sorption has to be monitored directly by changes in the solid phase, alternative a is inconvenient and prone to much greater errors compared to the usual technique of monitoring changes in solution concentration. Alternative b is somewhat of a hit-or-miss proposition. In the present study, we wish to estimate upper and lower limits of the shrinking gradient effect in order to reveal innate concentration effects on the real sorption process. To do this, two models are introduced.
On a kinetic level the time it takes to reach equilibrium depends on two processes: (a) the migration time, $\tau_M$, for molecules of sorbate to get from the liquid–solid interface to a sorption site inside the solid and (b) the time lag, $\tau_A$, associated with mass-transfer resistance at the site.

The model dealing with the first process (Wetting Front Model) assumes that $\tau_M \gg \tau_A$, so that sorption rate is dominated by migration time. In this case sorbate migration through the solid proceeds like a wetting front, with sorption behind the front always at equilibrium with solution and zero sorption ahead of the front. The wetting front model always underestimates the shrinking gradient effect.

The model dealing with the second process (Fast Diffusion Model) assumes that $\tau_A \gg \tau_M$, so that chemical is instantaneously homogeneous throughout the solid and sorption is limited by the time needed to overcome the mass-transfer resistance at the sorption site. The fast diffusion model always overestimates the shrinking gradient effect.

**Wetting Front Model.** Consider the soil as a population of sorption sites inside a solid. Let $q(t)$ be the fraction of total sorption sites behind the wetting front at time $t$. On the assumption that the Freundlich equation (eq 2) holds, sorption in the finite-bath case is given by

$$q^{\text{fin}}(t) = K_F C^{\text{fin}}(t)^N q^{\text{eq}}(t)$$  \hspace{1cm} (3)

where the superscript fin denotes the finite-bath case. We assume that both the infinite-bath case and the finite-bath case have the same equilibrium concentration of the solute in the ambient fluid, $C_e$. For the infinite-bath case $C(t)$ is a constant, $C_e$, and

- FIGURE 4. Sorption of phenanthrene to (a) Port Hueneme soil and (b) Pahokee soil for different initial dissolved concentrations. Curves are shown only to aid the eye.

- FIGURE 5. Normalized sorptive uptake of phenanthrene vs the square root of time. $Q_{\text{fin}}^\alpha$ (eq 8a) and $Q_{\text{fin}}^\alpha$ (eq 14) are theoretical limits on sorption for the infinite-bath case for (a) Port Hueneme soil ($C_0 = 0.998 \, \mu g/mL$) and (b) Pahokee soil ($C_0 = 0.386 \, \mu g/mL$).

$$Q^\alpha(t) = K_F(C_e)^N q^{\text{fin}}(t)$$  \hspace{1cm} (4)

where the superscript $\infty$ denotes the infinite-bath case.

For the finite-bath case simple mass balance dictates that

$$\frac{C_0 - C^{\text{fin}}(t)}{C_0 - C_e} = \frac{q^{\text{fin}}(t)}{q^{\text{eq}}}$$  \hspace{1cm} (5)

where $C_0$ is the initial aqueous concentration. Equation 5 can be rewritten as

$$C^{\text{fin}}(t) = C_e \left[ \alpha - (\alpha - 1)\frac{q^{\text{fin}}(t)}{q^{\text{eq}}} \right]$$  \hspace{1cm} (6)

to give the ambient liquid concentration in terms of the sorbed concentration and $\alpha$, the ratio of initial to final aqueous concentration ($\alpha = C_0/C_e$). By defining $Q$ as the normalized sorbed concentration (i.e., $Q^{\text{fin}}(t) = q^{\text{fin}}(t)/q^{\text{eq}}$ and $Q^\alpha(t) = q^\alpha(t)/q^{\text{eq}}$) and combining eqs 3 and 6, we obtain

$$Q^{\text{fin}}(t) = K_F C_e [\alpha - (\alpha - 1)Q^{\text{fin}}(t)]^N q^{\text{fin}}(t)$$  \hspace{1cm} (7)

A simple comparison of eqs 4 and 7 yields

$$Q^\alpha(t) = \frac{Q^{\text{fin}}(t)}{(\alpha - (\alpha - 1)Q^{\text{fin}}(t))^N q^{\text{fin}}(t)}$$  \hspace{1cm} (8)
The finite-bath example is characterized by transient sorption above the equilibrium value (Figure 6.4 in ref 22). The ratio $\frac{f(∞)(t)}{f(\text{fin})(t)}$ in eq 8 cannot, to the best of our knowledge, be solved in the nonlinear case, but the increased driving force due to this higher transient sorption causes $\frac{f(∞)(t)}{f(\text{fin})(t)}$ to always be less than unity. Thus, setting $\frac{f(∞)(t)}{f(\text{fin})(t)} = 1$ in eq 8 yields the following upper limit of sorption for the infinite-bath case given the finite-bath sorption curve:

$$Q(∞)(t) = \frac{Q(\text{fin})(t)}{\left[\alpha - (\alpha - 1)Q(\text{fin})(t)^N\right]}$$  \hspace{1cm} (8a)

For the case of a linear isotherm $N = 1$, eq 8a is equivalent to the transformation suggested by Ball and Roberts (24) to normalize the effect of differing solid to solution mass ratio. This transformation does not fold all of the sorption data onto one curve but rather, given the finite-bath sorption curve, results in an upper bound for the infinite-bath case. In general, the Wettling Front Model minimizes the shrinking gradient effect, whether or not the isotherm is linear, because only sites just in contact with the advancing front are subject to the changing solute activity in the liquid phase.

**Fast Diffusion Model.** In this case the rate of sorption should be proportional to the difference in activity of the chemical between the liquid and sorbed states; that is

$$\frac{\partial q(\text{fin})(t)}{\partial t} = k\{K_F C(\text{eq})[\alpha - (\alpha - 1)q(\text{fin})(t)^N - q(\text{fin})(t)]$$  \hspace{1cm} (9)

where $k$ is a rate constant. Combining eqs 9 and 6 we have

$$\frac{\partial q(\text{fin})(t)}{\partial t} = k\{K_F C(\text{eq})[\alpha - (\alpha - 1)Q(\text{fin})(t)^N - q(\text{fin})(t)]$$  \hspace{1cm} (10)

and dividing eq 10 by $K_F C(\text{eq})$ we obtain for the finite-bath case

$$\frac{\partial Q(\text{fin})(t)}{\partial t} = k\alpha [1 - Q(\text{fin})(t)]$$  \hspace{1cm} (11)

where $Q(\text{fin})(t)$ is the normalized sorption as defined above. We are looking for a lower bound for sorption in the infinite-bath case given the finite-bath sorption curve. Because $\alpha - (\alpha - 1)Q(\text{fin})(t) > 1$, to find the lower bound for sorption the Freundlich exponent $N$ in eq 11 is set to unity to give

$$\frac{\partial Q(\text{fin})(t)}{\partial t} = k\alpha [1 - Q(\text{fin})(t)]$$  \hspace{1cm} (12)

For the infinite-bath case the rate law is simply

$$\frac{\partial Q(\text{eq})(t)}{\partial t} = k\alpha [1 - Q(\text{eq})(t)]$$  \hspace{1cm} (13)

Dividing eq 12 by eq 13 and solving the resultant differential equation yields the lower limit infinite-bath sorption:

$$Q(\text{min})(t) = 1 - [1 - Q(\text{eq})(t)]^{1/\alpha}$$  \hspace{1cm} (14)

This Fast Diffusion case maximizes the shrinking gradient effect because all sites are immediately and continuously exposed to the solute activity in the liquid phase.

Figure 5 presents examples showing the effect of the transformations described by eqs 8a and 14 on the phenanthrene uptake data for Port Hueneme and Pahokee soils at initial concentrations of 0.998 and 0.363 μg/mL, respectively. As expected, the transformations resulted in slower rates of uptake for the infinite-bath compared to the finite-bath case. The real infinite-bath case will fall between the lines represented by the two models.

For both models the characteristic sorption time $\tau$ is computed as the first moment of the $Q(\text{eq})(t)$ vs. $t$ curve for each
soil and at several initial dissolved phenanthrene concentrations. The first moment was approximated by the expression

$$
\tau = \int_0^{\infty} \frac{dQ(t)}{dt} dt = t_{\text{final}} Q_{\text{final}}^n - \int_0^{t_{\text{final}}} Q^n(t) dt
$$

and the integral of the right-hand side was evaluated numerically. The upper bound for \( \tau \) is calculated by substituting \( Q_{\text{min}}^n \) (eq 14) into eq 15 and, in analogy, the lower bound for \( \tau \) is calculated by substituting \( Q_{\text{max}}^n \) (eq 8a) into eq 15.

Figure 6 shows graphs of the upper and lower bounds for \( \tau \) for seven soils as a function of the initial phenanthrene concentration. Solid lines are the result of performing linear regression through the points and are there only to facilitate visualization. Figure 6 suggests that both the upper and lower bounds of \( \tau \) decrease with increasing initial phenanthrene dissolved concentrations. This effect appears to be strongest in soils with a lower N. For Seal Beach soil (Figure 6g) with N = 1.019 the values of \( \tau \) are more scattered and the inverse relationship between \( \tau \) and initial dissolved concentration is not so evident. The same behavior is presented by Port Hueneme soil (Figure 6e) and to a lesser extent by modified Seal Beach soil (Figure 6f), for which N values are 0.91 and 0.921, respectively.

**Discussion**

This study proposes an alternative way to evaluate the rate of approach to sorptive equilibrium. It proposes a mathematical procedure for putting bounds on the shrinking gradient effect present in batch experiments when the compound sorbs nonlinearly and, thus, makes it possible to evaluate the intrinsic concentration dependence of sorption. Two types of experiments involving two compounds and seven soils show clearly that the time for attainment of sorptive equilibrium is concentration-dependent. It therefore agrees with the inferences of recent experimental work on soil and sediment materials (6, 12, 17, 21). The results further agree with theory and experiment on mesoporous reference materials (16) that the effective diffusion parameter is concentration-dependent when the isotherm is nonlinear.

The concentration dependence of the characteristic sorption time computed for infinite-bath conditions appears to be strongest for soils with Freundlich exponents \( N \leq 0.80 \) and weakest for soils with \( N > 0.90 \). The \( \tau \) calculated for Port Hueneme soil (\( N = 0.91 \)) was nearly independent of concentration. Although \( \tau \) for Seal Beach soil (\( N = 1.019 \)) seems to be concentration-dependent, the data are quite scattered and it is hard to say for sure. The presence of Bunker C oil contamination no doubt contributes to the linearity of the phenanthrene isotherm in Seal Beach soil. Removal of the oil by pentane extraction (modified Seal Beach) results in a lower N (0.921), increased values of \( \tau \), especially at lower concentration, and a steeper concentration dependence of \( \tau \) as compared with that of unextracted Seal Beach soil. These results make sense because the oil phase offers a linear partition domain where equilibrium is expected to be fairly rapid.

The origin of concentration-dependent kinetics is the nonuniform potential of the sorbent and the fact that molecular diffusion occurs in response to a chemical potential gradient. Figure 6 shows that \( \tau \) and its variation with initial dissolved concentration of solute are very different among the soils. Mechanisms associated with mass-transfer resistance include intraorganic matter diffusion and sorption-retarded diffusion through fixed pores (1). The variation in \( \tau \) may be due to the quality of organic matter, the size of organic matter particles, or the availability of shielded organic particles or coatings within the interstices of inorganic aggregates (28–30). If the latter is the case, the size of inorganic aggregates may be important. This study was not intended to help decide which of these processes is rate-limiting.

Pyrene takes longer to reach equilibrium than does a comparable concentration of phenanthrene, consistent with the differences in their molecular sizes and hydrophobicities. Molecular size is important for diffusion through a solid phase such as SOM or in micropores not much larger than the kinetic radius of the diffusing molecule, and hydrophobicity is important for diffusion in water-filled pores where sorption to the walls retards the progress of migration.

The infinite-bath \( \tau \) varies at most by a factor of 3 over a \( \sim 10^2 \) range in phenanthrene concentration for these soils. Although this seems to be small, bear in mind that \( \tau \) applies to the bulk of the contaminant. The contaminant may also include minor fractions that sorb by different mechanisms on different time scales that may be variously dependent on concentration. The findings of this study are significant in that they identify the confounding factor (shrinking gradient effect) likely to be responsible for much of the ambiguity in the literature concerning the concentration-dependent sorption kinetics of organic compounds. Furthermore, this study also provides the means for placing bounds on this experimental artifact.

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**Literature Cited**


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