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QUANTITATIVE STRUCTURE-ACTIVITY RELATIONSHIPS FOR EVALUATING THE INFLUENCE OF SORBATE STRUCTURE ON SORPTION OF ORGANIC COMPOUNDS BY SOIL

QINHONG HU, XIAOJIANG WANG and MARK L. BRUSSEAU*

Department of Soil and Water Science, University of Arizona, 429 Shantz, Tucson, Arizona 85721

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Abstract—The purpose of this work was to investigate the effect of sorbate structure, by using the quantitative structure-activity relationship (QSAR) approach, on sorption of organic compounds by two soils with different amounts of organic matter. Miscible displacement experiments were performed with several organic contaminants representing six classes of nonpolar, non-ionizable organic chemicals, including chlorinated aliphatics, chlorobenzenes, polycyclic aromatic hydrocarbons (PAHs), *n*-alkylbenzenes, methylated benzenes, and polychlorinated biphenyls (PCBs). The breakthrough curves were analyzed by using a bicontinuum model wherein sorption is assumed to be instantaneous for a fraction of the sorbent and rate limited for the remainder. The QSAR approach was used to investigate the dependency of both equilibrium and nonequilibrium sorption coefficients on topological descriptors representing structural properties of the solutes. For both equilibrium and nonequilibrium parameters, the first-order valence molecular connectivity ($^1\chi^V$) was found to be the best topological descriptor. Most of the rate-limited sorption behavior could be explained by accounting for the size and structure of the solute molecule, as indicated by the good correlation between the rate coefficient and $^1\chi^V$. This supports the contention that rate-limited sorption in these systems is controlled by a physical diffusion mechanism, consistent with the polymer diffusion model. Based on this model, the calculated diffusion-length ratios for the Borden and Mt. Lemmon soils, which have a large difference in organic-matter contents, compare favorably to the values determined from the measured rate data.

Keywords—Sorption QSAR Organic compounds Solute structure

INTRODUCTION

Rate-limited sorption of nonionic, low-polarity organic compounds by natural sorbents has been a focus of recent study [1-5]. Knowledge of the role of sorbate, solvent, and sorbent properties in mediating rate-limited sorption is required for a complete understanding of the sorption kinetics process. The structure of the sorbate (e.g., nature, size, and reactivity of functional groups) appears to have a major influence on the degree of rate-limited sorption experienced by a given sorbate [6-8]. Hence, the structure of the sorbate should be considered when the rate-limited sorption of organic chemicals is evaluated.

Quantitative structure-activity relationships (QSARs) are a means of evaluating the dependence of the behavior of solutes on their molecular properties. A QSAR analysis usually takes the form of a plot or regression of the properties of interest as a function of an appropriate molecular descriptor, which can be obtained from knowledge of molecular structure. Considerable effort has been devoted to using QSAR analysis to elucidate the fundamental molecular determinants of physical-chemical properties [9]. Sabljic [10,11] and Meylan et al. [12] demonstrated that molecular connectivity, a specific descriptor, can be a useful predictive tool of soil sorption coefficients for a wide range of organic chemicals. Despite the fact that the QSAR approach has been widely used

in many research areas, it has seldom been used to analyze rate-limited sorption of organic compounds by soil, either for parameter estimation or for mechanism evaluation [8].

The purpose of this work was to investigate the relationship between sorbate structure and rate-limited sorption by using the QSAR approach. This is accomplished by examining the rate-limited sorption of compounds, representing six classes of major organic contaminants, by two sorbents differing in organic-matter contents. Both equilibrium and rate-limited sorption parameters are correlated with topological descriptors to gain more information about the attendant sorption processes.

MATERIALS AND METHODS

Materials

The following analytical-grade chemicals (Aldrich Chemical Co.) were employed in the experiments: pentafluorobenzoate, trichloroethene, tetrachloroethene, chlorobenzene, 1,2,4-trichlorobenzene, benzene, naphthalene, anthracene, pyrene, toluene, *m*-xylene, ethylbenzene, *n*-propylbenzene, *n*-butylbenzene, biphenyl, and 2-chlorobiphenyl.

Two porous materials were used for this study. One (Borden) is a sandy subsoil collected from the Canadian Air Force base in Borden, Ontario. The second (Mt. Lemmon) is a surface soil collected from a site near Tucson, Arizona. Measured organic-carbon contents and particle-size distributions are reported in Table 1. Both soils were air-dried and sieved (<2 mm) prior to use.

*To whom correspondence may be addressed.

Table 1. Properties of soils and columns

Soil	Particle-size distribution (%)			Organic carbon (%)	Bulk density (g/cm ³)	Porosity (cm ³ /cm ³)	Column length (cm)	Column pore volume (ml)
	Sand	Silt	Clay					
Borden	98	1	1	0.29	1.69	0.41	7.0	10.0
Mt. Lemmon	60.3	24.0	15.7	12.6	0.81	0.73	5.0	18.4

Preparative chromatography columns made of precision-bore borosilicate glass (2.5 cm i.d., 5.0 cm length, Kontes Co.) or precision-bore stainless steel (2.1 cm i.d., and 7.0 cm length, Alltech Associates Inc.) were used in the experiments. The columns are designed to have a minimum void volume in the end plates.

Experimental procedures

The columns were packed in incremental steps with the dry porous medium to establish uniform bulk density. After packing, the columns were slowly wetted from the bottom with electrolyte solution (0.01 N CaCl₂). After saturation was achieved, about 100 pore volumes of solution were pumped through the columns to condition them to the electrolyte solution. Selected properties of the packed columns are reported in Table 1. The unusually small bulk density and large porosity associated with the Mt. Lemmon soil results primarily from its large organic-carbon content.

The apparatus and methods employed for the miscible displacement studies were similar to those used by Hu and

Brusseau [13]. One single-piston HPLC pump (Gilson Medical Electronics, model 305) was connected to the column, with a three-way switching valve placed in-line to facilitate switching between solutions with and without the solute of interest. The system was designed so that the solutes contacted only stainless steel, glass, or Teflon.

A flow-through, variable-wavelength UV detector (Gilson, model 115) was used to continuously monitor concentrations of most compounds. The wavelength, determined by selecting for maximum response, used for each compound is reported in Table 2. A flow-through fluorometer (Gilson, model 121) was used for the anthracene and pyrene experiments (excitation filter, 305–395 nm; emission filter, 430–470 nm). Output of the flow-through experiments was recorded on a strip-chart recorder (Fisher Recordall Series 5000).

A flow rate of 1.6 ml/min was used for all experiments. This corresponded to pore-water velocities of approximately 60 and 27 cm/h for the Borden and Mt. Lemmon columns, respectively. Pentafluorobenzoate, which was not sorbed by either of the two soils, was used to characterize the hydrodynamic characteristics of the columns. The initial con-

Table 2. Physicochemical properties of compounds

Chemical ^a	Log K _{ow} ^b	λ ^c (nm)	C ₀ (mg/L)	TSA ^d (nm ²)	VWV ^e (cm ³ /mol)	χ ^f
TCE	2.29	225	30	1.11	49.20	2.075
PCE	2.60	225	30	1.28	57.80	2.514
CB	2.84	261	100	1.27	57.84	2.476
TCB	4.28	225	s.s. ^f	1.60	76.80	3.436
BNZ	2.13	256	100	1.10	48.36	2.000
NAP	3.35	225	10	1.56	73.96	3.405
ANT	4.54	FL ^g	s.s.	2.02	99.56	4.809
PYN	4.88	FL	s.s.	2.13	109.04	5.559
TOL	2.73	261	100	1.27	59.51	2.411
mXYL	3.13	261	100	1.50	70.66	2.824
eBNZ	3.15	261	100	1.45	69.74	2.971
pBNZ	3.69	257	100	1.63	79.97	3.471
bBNZ	4.26	258	s.s.	1.81	90.20	3.971
BIP	4.09	250	5	1.82	90.08	4.071
2PCB	4.51	215	s.s.	1.95	99.56	4.265

^aTCE, trichloroethene; PCE, tetrachloroethene; CB, chlorobenzene; TCB, 1,2,4-trichlorobenzene; BNZ, benzene; NAP, naphthalene; ANT, anthracene; PYN, pyrene; TOL, toluene; mXYL, *m*-xylene; eBNZ, ethylbenzene; pBNZ, *n*-propylbenzene; bBNZ, *n*-butylbenzene; BIP, biphenyl; 2PCB, 2-chlorobiphenyl.

^bFrom Brusseau [8] and Hanai and Hubert [19].

^cλ, the UV wavelength used.

^dTSA, total molecular surface area, from Woodburn et al. [20] and Okouchi et al. [21].

^eVWV, van der Waals volume, from Hanai and Hubert [19] and Kamlet et al. [22].

^fs.s., denotes solution saturated to aqueous solubility limit.

^gFL, measured by flow-through fluorometer.

centrations of solutes used in the experiments are listed in Table 2.

Data analysis

A bicontinuum model based on first-order mass transfer was used to analyze results of the experiments. With the first-order model, sorption is conceptualized to occur in two domains (see references in [4]):



where

$$S_1 = FK_p C \quad (2)$$

$$dS_2/dt = k_1 S_1 - k_2 S_2 \quad (3)$$

and where C is the solution-phase solute concentration (ML^{-3}); S_1 is the sorbed-phase concentration (M M^{-1}) in the "instantaneous" domain; S_2 is the sorbed-phase concentration (M M^{-1}) in the rate-limited domain; K_p is the linear equilibrium sorption coefficient ($\text{L}^3 \text{M}^{-1}$); F is the fraction of sorbent for which sorption is instantaneous; t is time (T), and k_1 and k_2 are forward and reverse first-order rate coefficients (T^{-1}), respectively.

The following nondimensional equations describe the transport of sorbing solutes during one-dimensional, steady-state water flow in a homogeneous porous medium:

$$\beta R \frac{\partial C^*}{\partial T} + (1 - \beta)R \frac{\partial S^*}{\partial T} = \frac{1}{P} \frac{\partial^2 C^*}{\partial X^2} - \frac{\partial C^*}{\partial X} \quad (4)$$

$$(1 - \beta)R \frac{\partial S^*}{\partial T} = \omega(C^* - S^*) \quad (5)$$

The definitions for Equations 4 and 5 are as follows:

$$C^* = C/C_0 \quad (6a)$$

$$P = vL/D \quad (6b)$$

$$S^* = S_2/(1 - F)K_p C_0 \quad (6c)$$

$$R = 1 + (\rho/\theta)K_p \quad (6d)$$

$$T = vt/L \quad (6e)$$

$$\beta = [1 + F(\rho/\theta)K_p]/R \quad (6f)$$

$$X = x/L \quad (6g)$$

$$\omega = k_2(1 - \beta)RL/v \quad (6h)$$

and where C_0 is the solute concentration (M L^{-3}) of the influent solution; v is the average pore-water velocity (L T^{-1}) (with $v = q/\theta$); q is Darcy flux (L T^{-1}); x is distance; L is column length; D is the dispersion coefficient ($\text{L}^2 \text{T}^{-1}$); ρ is soil bulk density (M L^{-3}); θ is fractional volumetric soil

water content; P is the Peclet number, which represents the dispersive-flux contribution to transport; R is the retardation factor, which represents the effect of sorption on transport; β is the fraction of instantaneous retardation; and ω is the Damköhler number, which is a ratio of hydrodynamic residence time to characteristic time for sorption. These last two terms specify the degree of nonequilibrium existent in the system, which decreases as either of the two increase in magnitude.

To run the model, knowledge of the following parameters is required: P , R , β , ω , and T_0 , the size of the input solute pulse in pore volumes. The value for P was obtained from the breakthrough curve of a nonsorbing solute, pentafluorobenzoate, by use of a nonlinear, least-squares optimization program [14] to solve the advective-dispersive local equilibrium transport model. The value for R , and thus K_p (see Equation 6d), was obtained by moment analysis. The size of the solute pulse, T_0 is known from measurement. The two unknown parameters are thus β and ω . A nonlinear, least-squares optimization program using the bicontinuum model [14] was used under flux-type boundary conditions to determine values for the two unknowns. Values for F and k_2 were calculated from the values of β and ω (see Equations 6f and 6h). When R is small, the optimization often produced F values less than 0. In these cases, the optimization was redone with F set equal to 0, which results in fixed values for β ($= 1/R$). This parameterization is equivalent to the so-called one-site model, where all sorption is rate-limited.

Molecular descriptors

Three size- and shape-related molecular descriptors are used in the QSAR analyses. The first is the first-order valence molecular connectivity index ($^1\chi^v$) (the sum over all connections or edges in the hydrogen-suppressed molecular graph), which is a representation of the topological size of the molecule and its degree of branching. Values for $^1\chi^v$ are calculated by using the Randic algorithm, which is described in Kier and Hall [15]. The second is total molecular surface area (TSA) (the sum of individual atoms or group surface area contributions), which represents the maximum amount of contact that a molecule can have with its surrounding environment. The third is van der Waals volume (VWV) (calculated from the van der Waals radii of the atoms of which the molecule is composed), which is another measure of the size of a molecule. Values for TSA, VWV, and $^1\chi^v$ of all compounds used in the experiments are reported in Table 2.

RESULTS AND DISCUSSION

Transport and sorption data

The breakthrough curve for pentafluorobenzoate was symmetrical, whereas those for the sorbing solutes were asymmetrical and exhibited some degree of "tailing," or delayed approach to $C/C_0 = 1$ or 0. This behavior suggests that the nonequilibrium is caused by a sorption-related rather than a transport-related mechanism [4,7]. Representative breakthrough curves for transport of organic compounds in the two soils are shown in Figure 1. Note that while only the frontal curves are presented for illustration and comparison, the sorption parameters are obtained from analysis of the

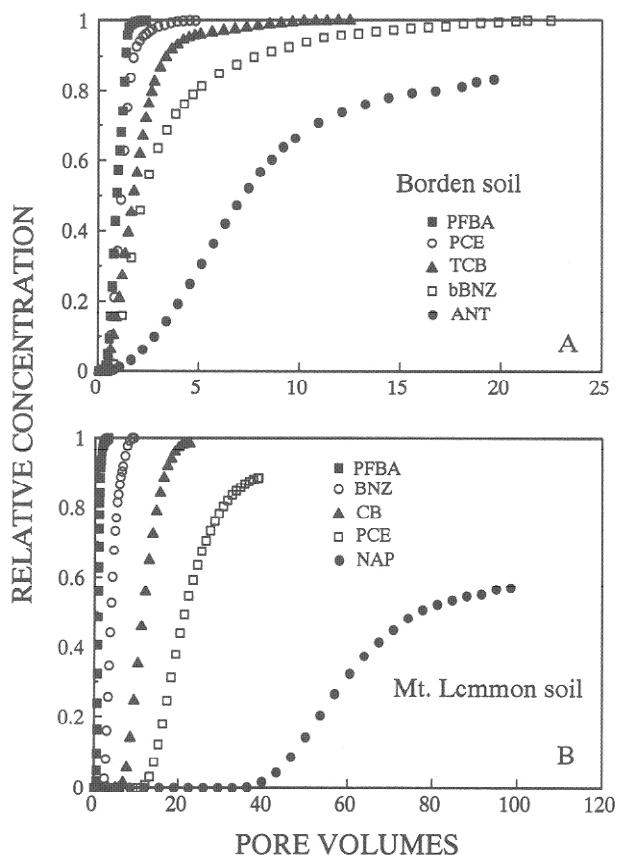


Fig. 1. Representative breakthrough curves for transport of organic compounds in Borden and Mt. Lemmon soils.

complete breakthrough curves. Examples of the simulations produced with the bicontinuum model are presented in Figure 2. The optimized simulations closely match the experimental results, confirming that the bicontinuum model describes quite well sorption and transport in the miscible displacement experiments. Values for F and k_2 obtained from optimization of the breakthrough curves are reported in Table 3.

The relationship between sorption kinetics and equilibrium sorption has been quantified by Brusseau and Rao [16], who analyzed literature data using the linear free-energy relationship (LFER) approach. The functionality has since been substantiated by experiments [6, 7]. A plot of the reverse rate coefficient (k_2) versus the equilibrium-sorption coefficient (K_p) is provided in Figure 3 for the Borden and Mt. Lemmon soils. The geometric mean functional (GMF) regression method discussed by Halfon [17] was employed to obtain the regression equation. This analytical procedure accounts for uncertainty in the independent, as well as the dependent, variable. Because both k_2 and K_p have associated error, it is more appropriate to use the GMF regression method for the $k_2 - K_p$ relationship [16].

The inverse nature of the $k_2 - K_p$ relationship presented in Figure 3 suggests that a diffusion-limited mechanism is re-

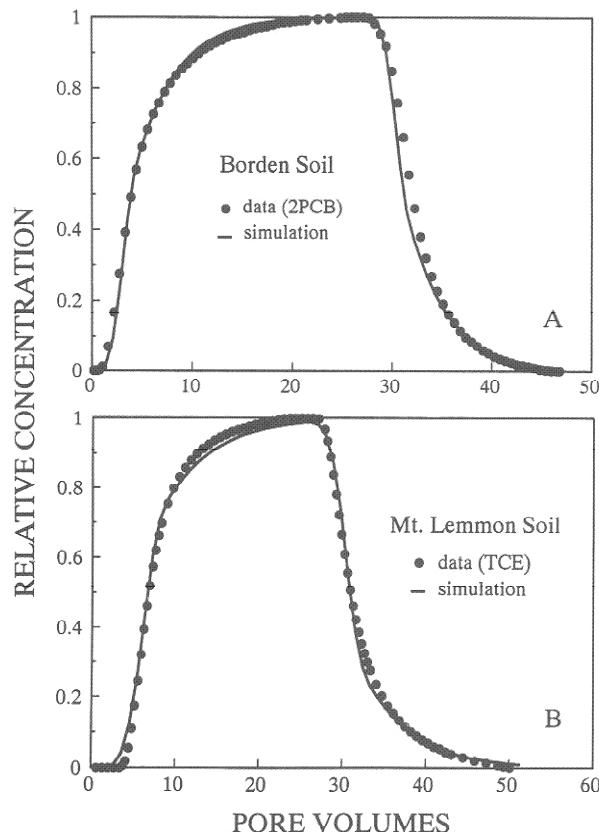


Fig. 2. Representative breakthrough curves (data points) and simulations produced with the bicontinuum model (solid lines) for Borden and Mt. Lemmon soils.

sponsible for the observed nonequilibrium. Recent research [6–8] has shown that diffusion within the matrix of sorbent organic matter, or intraorganic matter diffusion, appears to be responsible for the rate-limited sorption of low-polarity organic compounds by nonaggregated sorbents containing moderate levels of organic matter (e.g., >0.1%). A model that interprets rate-limited sorption in terms of diffusion of sorbate within a polymeric structure was presented by Brusseau et al. [6]. The model relates the first-order reverse rate coefficient to a polymer diffusivity as follows:

$$k_2(1 - F) = \alpha = aD/l^2 \quad (7)$$

where α is a mass-transfer constant (T^{-1}); a is a shape factor for the diffusion domain; D is the diffusion coefficient ($L T^{-2}$) in the polymer; and l is the characteristic diffusion length (L). The log-log-linear inverse relationship that exists between k_2 and K_p is a reflection of the strong dependency of D on molecular size of the sorbate [6].

The structure of the diffusing molecule can have a major impact on diffusion in polymeric-type materials. Substituted molecules (e.g., benzene with various functional groups), for example, have been shown to have smaller D values in comparison to unsubstituted molecules. The addition of

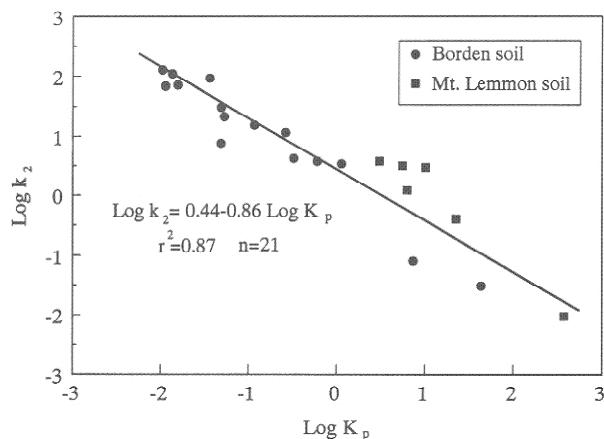


Fig. 3. Relationship between the first-order reverse-rate coefficient (k_2 , h^{-1}) and the equilibrium-sorption coefficient (K_p , ml g^{-1}) for Borden and Mt. Lemmon soils.

functional groups results in an increased potential for entanglement with the polymer mesh, which will constrain diffusion. Quantitative structure-activity relationship analysis can be used to examine the influence of solute structure on diffusion-controlled processes.

QSAR for equilibrium sorption

The relationships between the equilibrium-sorption coefficient (K_p) and the molecular descriptors (TSA, VWV, and $^1\chi^v$) are determined by regression. The extent of goodness of fit, based on the correlation coefficients in this case, shows the following order: $^1\chi^v > \text{TSA} > \text{VWV}$. Correlations between K_p and $^1\chi^v$ or VWV for the soils are shown in Figure 4 for illustration. The correlation between K_p and $^1\chi^v$ is quite good ($r^2 = 0.94$ for Borden soil and 0.93 for Mt. Lemmon soil, respectively), considering the fact that several classes of organic compounds were used in the study. Con-

versely, the correlation between K_p and VWV is not as good ($r^2 = 0.88$ for Borden soil and 0.83 for Mt. Lemmon soil, respectively). Note that the trend is the same for two soils with quite different amounts of organic matter.

Molecular connectivity describes primarily the size and structure of molecules. The first-order molecular connectivity was found to be useful for describing the interaction of a variety of major organic contaminants with organic matter in soil and sediments [10–12,18]. The index produces more accurate estimates of K_{oc} , is easier to use, and is more comprehensive in its coverage of structurally diverse organic compounds than other K_{oc} estimation methods [12]. Sabljic [11] stated that direct correspondence between molecular structure and the molecular connectivity makes it possible to locate structural features responsible for environmental behavior of organic contaminants in the soil and to learn more about the underlying mechanism(s) of sorption processes at the molecular level.

The effect of the molecular configuration of the sorbate on equilibrium sorption was probed with several alkylbenzenes. Correlations between the equilibrium sorption coefficients and $^1\chi^v$ or VWV for six classes of organic chemicals are provided in Figure 5 for the Borden soil. The baseline for the unsubstituted aromatic hydrocarbons (UAHs) was established by regression of the series: benzene, anthracene, and pyrene. Note the UAH lines in Figure 5 do not include the naphthalene data point, which appears to be an outlier.

The impact of additions of one or two chlorine or methyl groups was evaluated by using toluene, *m*-xylene, and chlorobenzenes. Apparently, the addition of small numbers of the functional groups does not result in behavior deviating from the UAH line (see Fig. 5). The *n*-alkylbenzene group (and trichlorobenzene, biphenyl, 2-chlorobiphenyl) diverges below the line representing the UAHs. Similar results were reported previously [8]. The difference in K_p vs. $^1\chi^v$ and K_p vs. VWV relationship is the extent of separation between the UAH and alkylbenzene groups. The molecular connectivity index appears to account for more of the behavior, as quan-

Table 3. Parameter values for soil data

Chemical	Borden soil				Mt. Lemmon soil			
	K_p (ml/g)	k_2 (1/h)	F	α (1/h)	K_p (ml/g)	k_2 (1/h)	F	α (1/h)
TCE	0.011	68.4	0	68.4	6.33	1.21	0.70	0.37
PCE	0.053	21.4	0.63	7.98	22.60	0.40	0.72	0.11
CB	0.014	110.2	0	110.2	10.20	2.95	0.85	0.43
TCB	0.26	11.6	0.27	8.46				
BNZ	0.011	127.0	0	127.0	3.10	3.73	0.75	0.94
NAP	0.049	7.57	0	7.57	377.80	0.0094	0.15	0.008
ANT	7.46	0.08	0.26	0.06				
PYN	43.50	0.030	0.14	0.03				
TOL	0.016	71.5	0	71.5	5.62	3.14	0.72	0.87
<i>m</i> XYL	0.049	30.8	0	30.8				
eBNZ	0.036	92.6	0	92.6				
pBNZ	0.12	15.4	0.16	13.0				
bBNZ	0.61	3.76	0.27	2.76				
BIP	0.33	4.19	0.55	1.87				
2PCB	1.14	3.40	0.50	1.69				

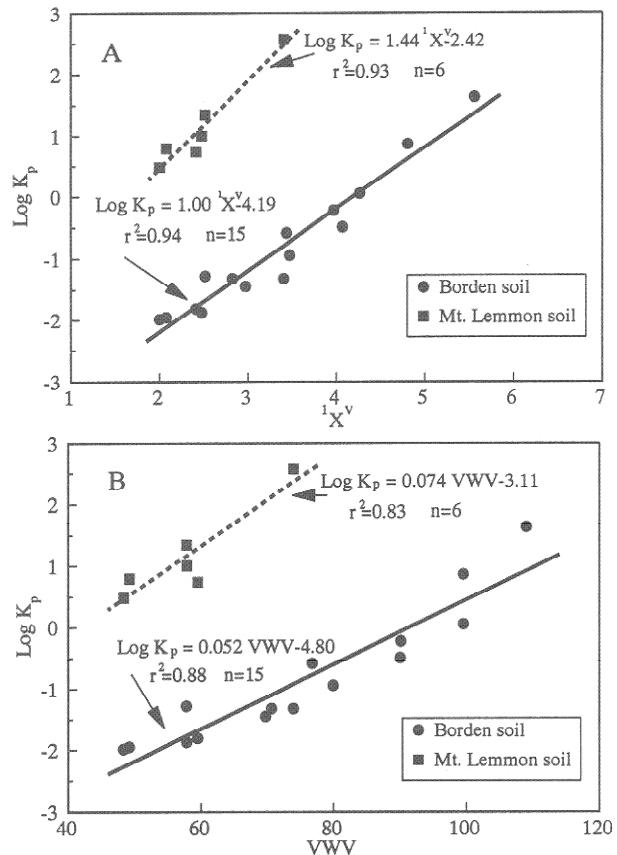


Fig. 4. (A) Correlation between equilibrium sorption coefficient (K_p) and first-order valence molecular connectivity index (${}^4\chi^v$) for Borden and Mt. Lemmon soils. (B) Correlation between equilibrium sorption coefficient (K_p) and van der Waals volume (VWW) for Borden and Mt. Lemmon soils.

tified by the respective r^2 values in Figure 4. This suggests that ${}^4\chi^v$ is a better descriptor for sorption of these compounds.

QSAR for rate-limited sorption

The mass-transfer coefficient (α) is used in the analyses of the rate-limited sorption data because the length of the diffusion path is unknown. Because each of the two data sets was collected by using one sorbent, the sorbent-related parameters (a, l) may be assumed to be constant within each data set. Hence, use of α should be equivalent to using the diffusion coefficient (see Eq. 7). The use of α also allows scaling of diffusion-based data and first-order-based data to a common parameter, thus facilitating direct comparison [8].

The relationships between the mass-transfer coefficient (α) and the molecular descriptors (TSA, VWV, and ${}^4\chi^v$) were evaluated by regression analysis. The inverse correlations between α and ${}^4\chi^v$ or VWV are shown in Figure 6. The goodness of fit, based on the correlation coefficients, shows the following order: ${}^4\chi^v > \text{TSA} > \text{VWW}$, which is the same as that observed for the equilibrium-sorption coefficient. The correlation between α and ${}^4\chi^v$ is good ($r^2 = 0.88$

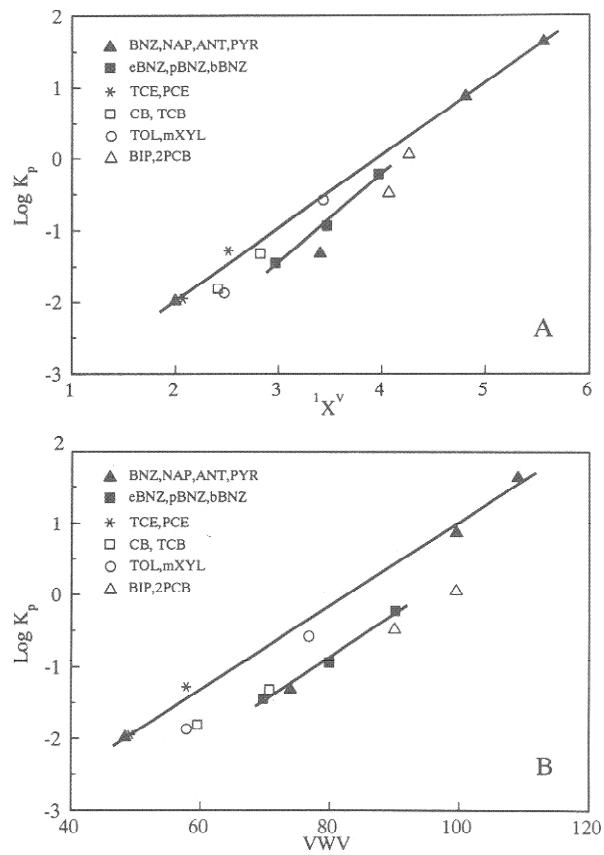


Fig. 5. (A) Correlation between equilibrium sorption coefficient (K_p) and first-order valence molecular connectivity index (${}^4\chi^v$) for organic compounds in Borden soil. (B) Correlation between equilibrium sorption coefficient (K_p) and van der Waals volume (VWW) for organic compounds in Borden soil.

for Borden soil and 0.83 for Mt. Lemmon soil), considering the range of classes of organic compounds. Conversely, the correlation between α and VWV is not as good ($r^2 = 0.79$ for Borden soil and 0.70 for Mt. Lemmon soil). The present QSAR analysis shows that the rate-limited sorption of organic compounds by these soils is primarily influenced by the size and structure of the molecule, which is best described by the ${}^4\chi^v$ descriptor.

Correlations between the mass-transfer coefficient α and ${}^4\chi^v$ or VWV for six classes of organic chemicals are presented in Figure 7 for the Borden soil. Apparently, the addition of small numbers of chlorine or methyl groups does not result in behavior deviating from the UAH line. Conversely, the *n*-alkylbenzene group (and trichlorobenzene, biphenyl, 2-chlorobiphenyl) diverges above the line representing the UAHs. As for the K_p case, the difference between the α vs. ${}^4\chi^v$ and ${}^4\chi^v$ vs. VWV relationships is the extent of separation between the UAH and alkylbenzenes groups. Again, ${}^4\chi^v$ appears to be a better descriptor of sorption dynamics.

The results discussed above are comparable to those obtained previously [8]. This is illustrated in Figure 8, where the

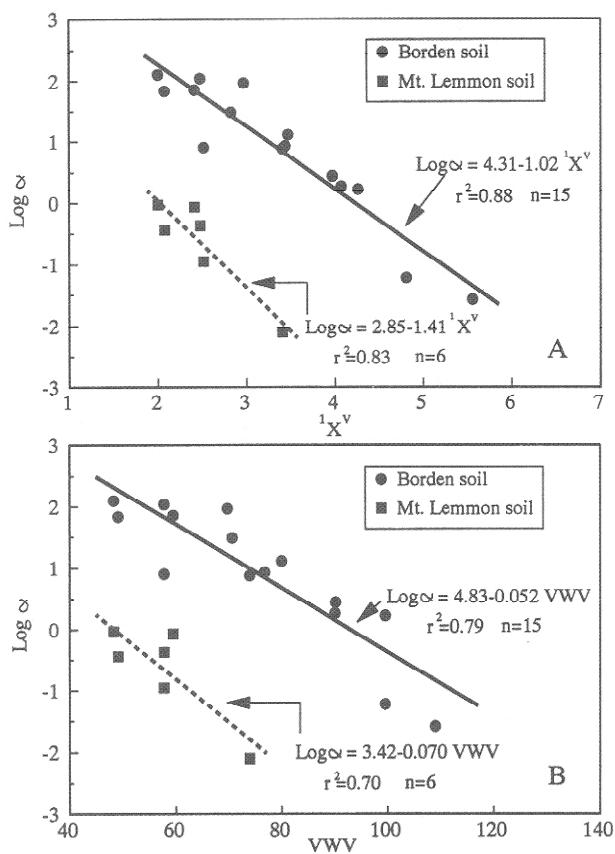


Fig. 6. (A) Correlation between mass-transfer coefficient (α) and first-order valence molecular connectivity index ($^1X^v$) for Borden and Mt. Lemmon soils. (B) Correlation between mass-transfer coefficient (α) and van der Waals volume (VWV) for Borden and Mt. Lemmon soils.

results obtained by Brusseau [8] for two soils with moderate organic-matter contents (between 1% and 0.1%) are plotted with the results of the present work. The data for the Borden soil are approximately grouped with the two literature data sets. Thus, the data for the three soils with similar organic-matter contents are grouped separately from the data for the soil with a much larger organic-matter content.

Estimation of diffusion-path lengths

The length of the diffusion path associated with the observed rate-limited sorption behavior can be estimated for the two soils. In this particular case, organic matter appears to be the most likely diffusion medium. Assuming soil-particle and organic-matter densities of 2.5 g/cm^3 and 1.0 g/cm^3 , respectively, the volume ratio between organic matter and soil particles can be calculated for the two soils with knowledge of the respective organic-matter contents. The thickness of a shell of organic matter covering the soil particle (assumed to be spherical) can then be calculated based on the estimated effective particle diameter for the soil. Based on an effective particle diameter of $100 \mu\text{m}$ (very fine sand) for Mt. Lem-

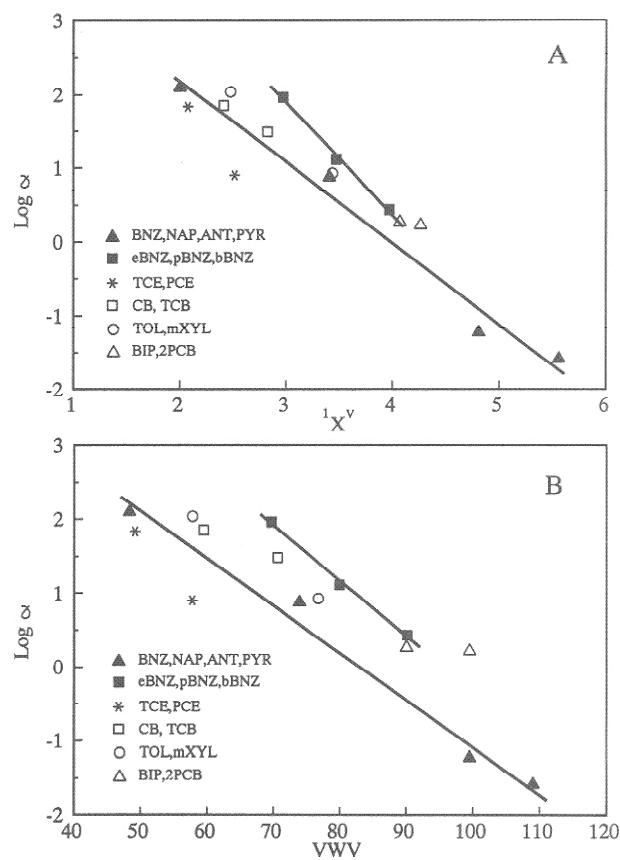


Fig. 7. (A) Correlation between mass-transfer coefficient (α) and first-order valence molecular connectivity index ($^1X^v$) for organic compounds in Borden soil. (B) Correlation between mass-transfer coefficient (α) and van der Waals volume (VWV) for organic compounds in Borden soil.

mon soil, l_M is calculated to be $11.5 \mu\text{m}$. With an effective particle diameter of $600 \mu\text{m}$ (coarse sand) for Borden soil, l_B is calculated to be $1 \mu\text{m}$. The l_M/l_B ratio is 11.5 based on these calculations.

The value for l_M/l_B calculated above can be compared to a value that can be obtained from analysis of the α data reported in Table 3. Assuming that the shape factor a and the "polymeric" diffusion coefficient are the same for the same sorbate in the two sorbents, Equation 8 can be derived from Equation 7:

$$\Delta \log \alpha = \log \alpha_B - \log \alpha_M = 2 \log l_M - 2 \log l_B \quad (8)$$

where subscripts B and M denote Borden and Mt. Lemmon soil, respectively. The average l_M/l_B ratio calculated from the α data reported in Table 3 for six sorbates among two soils is 13.5 ± 1.6 ($\Delta \log \alpha = 2.26 \pm 0.41$). This value is quite comparable to the ratio determined from the measured soil properties. Of course, these results are limited by the validity of the assumptions used. For example, we do not expect soil organic matter to be distributed as a continuous film on

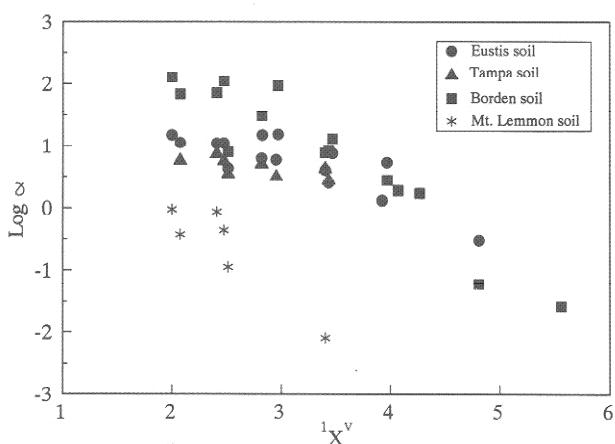


Fig. 8. Correlation between mass-transfer coefficient (α) and first-order valence molecular connectivity index (${}^1\chi^v$) for Borden, Eustis, Tampa, and Mt. Lemmon soils.

the soil particle. However, it is encouraging that the application of the diffusion-based first-order kinetics model provides results that are seemingly consistent with measured soil properties.

SUMMARY AND CONCLUSIONS

The QSAR approach was used to investigate the dependency of both equilibrium and rate-limited sorption coefficients for low-polarity organic compounds on topological descriptors (e.g., ${}^1\chi^v$, TSA, and VWV) representing structural properties of the sorbates. For both equilibrium and rate-limited parameters, the first-order valence molecular connectivity ${}^1\chi^v$ is found to be the best topological descriptor. Most of the rate-limited sorption behavior can be explained by accounting for the size and structure of the solute molecule, as indicated by the good correlation between α and ${}^1\chi^v$. These results support the contention that rate-limited sorption is controlled by a physical-diffusion mechanism, consistent with the polymer-diffusion model. Based on this model, the calculated diffusion-length ratios for the Borden and Mt. Lemmon soils, which have a large difference in organic-matter contents, compare favorably to the values determined from the measured rate data.

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