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Modeling Short-Term Soil−Water Distribution of Aromatic Amines

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The applicability of a distributed parameter model for describing the distribution of aniline and α-naphthylamine between soil and aqueous phases at short contact times was assessed. Mass action equations considered in the distributed parameter model were (a) acid dissociation of the protonated organic amine (BH^+); (b) sorption of the neutral species (B) to soil organic carbon through the partition coefficient K_{oc}; and (c) ion exchange of the protonated organic amine and inorganic divalent cations ($Ca^{2+} + Mg^{2+} = D^{2+}$). The last reaction was expressed mathematically as separated association reactions for each cation to unoccupied cation exchange sites, with constants K_{BH} and K_D. A Gaussian distribution on log K_{BH} values with mode μ and standard deviation σ was employed. The overall model was expressed as a system of two nonlinear equations with two unknown values (BH^+ and D^{2+}). The model was evaluated with aniline and α-naphthylamine isotherms measured on three Indiana soils ranging in pH (4.5−7.0) and added calcium concentration (0.5−50 mM) after a 24 h contact period. The parameters K_{oc}, μ, and σ for each amine were obtained by minimizing the sum of squared residuals between predicted and measured aqueous-phase organic amine concentrations (i.e., $[B]_{aq} + [BH^+]_{aq}$) for all soil, pH, and $CaCl_2$ conditions, simultaneously. Calculated isotherms were compared against those calculated with the general form of the speciation model in which a singular value of K_{BH} was employed. The distributed parameter form of the model resulted in nonlinear calculated isotherms in general agreement with the curvature of α-naphthylamine measured isotherms. Skewed distributions on log K_{BH} were evaluated also.

Introduction

Organic amines such as aniline and aniline derivatives are important environmental contaminants because of the combined effects of their high potential toxicity and carcinogenicity (*1*) and the large mass of them produced each year. These organic bases are employed as starting materials in the industrial manufacturing of synthetic chemicals such as dyes, pesticides, varnishes, and perfumes (*1, 2*). Anilines also are found in wastes from coal gasification and shale oil extraction processes (*3, 4*), and as microbial degradation products in soils treated with phenylamide herbicides (*5*).

The environmental transport and fate of these chemicals is partially determined by soil−water mass-transfer processes. Due to pH-dependent speciation of organic amines and the difference in the physicochemical properties of the species, mass transfer from water to specific or nonspecific soil constituent sites is greatly affected by pH. Under alkaline conditions, many organic amines exist predominately in their nonionic form, and mass transfer occurs through hydrophobic interactions (*6*−*9*). Greater sorption generally is observed at lower pH values (*10*) where the conjugate acid is in significant amounts, with cation exchange as the dominant mechanism under these conditions (*11*). The wide variety of functional groups (carboxylates, phenolates, silicates, iron and aluminum oxides, benzoates, etc.) present as ligands on soil, range in their affinities for protons and other cations including protonated organic amines (*12−14*). Some ligands and cations associate very strongly as inner-sphere complexes and some associate very weakly due to attractive forces occurring through hydration spheres and across other solvent molecules (i.e., through a diffuse layer).

Several methods are available to represent the frequency of soil sites through which association occurs. Two basic types of frequency models exist: discrete and continuous. For a discrete frequency, the composite sorption isotherm is represented as a linear superposition of an isotherm equation over *N* different independent sites (*15*). In the case of a linear isotherm, the discrete frequency is represented by

$$q(C) = \sum_{j=1}^{j=n} [S_j q_j(C, K_j)] \tag{1}$$

where $q(C)$ (mol/kg) is the average sorbed phase concentration, C (mol/L) is the aqueous-phase single solute concentration, S_j is the concentration of subset j sorption sites with affinity or sorption constant K_j (L/mol), and q_j (C, K_j) is a local and energetically homogeneous isotherm sorbed phase concentration (i.e., $= CK_j$ in the case of a linear isotherm). As $N \rightarrow \infty$, S_j approaches a continuous frequency distribution, expressed in eq 2 as a function of log K rather than K

$$q(C) = \int_{\log K_{\min}}^{\log K_{\max}} q(C, \log K) f(\log K) d \log K \tag{2}$$

Equations 1 and 2 or variations on them have been employed to model diverse environmental systems. For example, Perdue et al. (*12, 13*) employed a bimodal Gaussian distribution expression to model the binding of protons and metal ions to carboxyl and phenolic ligands on humic substances. The association reaction employed was Langmuir-type complexation of the metal (or proton) to a deprotonated ligand on the humic substances. Only 1:1 metal−ligand complexes were considered. Schiewer and Volesky (*16*) used a similar but simpler approach to model proton−metal ion exchange on biomass. They considered two classes of ligands (carboxyl and sulfate groups) and simple complexation reactions with 2:1 stoichiometry in their model. No distributed parameters were employed (constant *K* within each ligand class). Brown and Combs (*14*) used a multicomponent Langmuir equation to predict the sorption of methylacridinium ion in the presence of competing inorganic cations. Weber et al. (*17*) used a distributed reactivity model to predict the sorption of neutral organic compounds to soils and sediments. These authors modeled the sorption process as the sum of discrete linear and nonlinear (i.e., Freundlich) functions to represent energetic differences between or within individual elements. Brownawell et al. (*18*) employed a

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TABLE 1. Selected Physical and Chemical Properties of the Organic Amines Employed

chemical	MW^a (g/mol)	pK_a^{a}	S_w^{a} (mg/L)	log K_{ow}	log K_{oc}
aniline	93.1	4.63	34 000	0.90^a	1.41^b
α-naphthylamine	143.2	3.92	1700	2.22,^{a} 2.25^c	2.24^b

[a] Lee et al. (*32*), S_w is aqueous solubility. [b] Calculated by log $K_{oc} = 0.85 + 0.62$ log K_{ow} [Sabljic et al. (*33*)]. [c] Sablijic et al. (*33*).

discrete multisite competitive adsorption model to describe the adsorption of organic cations to different natural adsorbents. Two different types of sites were defined for the two sorption mechanisms considered: cation exchange and hydrophobic-like sorption of the organic cation.

In this study, we have utilized a continuous frequency distribution (i.e., distributed parameter) to describe the transfer of monovalent organic cations to water-saturated soils and have incorporated the associated algorithms into an overall speciation model. Although this approach is more computationally intense than common discrete approaches, we present several conventions that formalize the solution for easy implementation.

Model Development

A discrete two-site (TS) model and a distributed parameter (DP) model are developed, contrasted, and evaluated with experimental data. The TS model is a general mass action model that does not consider site heterogeneity of cation exchange sites, and the DP model allows for varying affinities of cation-exchange sites for BH^+.

Two-Site Model. The two-site mass action model considers the following chemical reactions and mass transfer processes: (i) association of organic bases with protons in water (eq 3); (ii) mass transfer of the neutral form of the organic amines (B) to soil organic matter (eq 4); and (iii) cation exchange between inorganic cations (Ca^{2+}, Mg^{2+}) and organic cations (BH^+) to sites on the soils (eq 5),

$$K_a = \frac{[B]_{aq}[H^+]_{aq}}{[BH^+]_{aq}} \tag{3}$$

$$K_d = f_{oc}K_{oc} = \frac{[B]_s}{[B]_{aq}} \tag{4}$$

$$K_G = \frac{[BHS][D^{2+}]_{aq}^{0.5}}{[BH^+]_{aq}[D_{0.5}S]} \tag{5}$$

where K_a is the acid dissociation constant of the conjugate acid (mol/L), $[B]_{aq}$ is the aqueous neutral organic amine (mol/L), K_{oc} is the partition coefficient of B to soil organic carbon (L/kg), f_{oc} is the fraction of organic carbon, $[B]_s$ is the concentration of B associated with the soil (mol/kg), K_G is the selectivity coefficient employing the Gapon cation-exchange convention ($M^{-0.5}$) (*19*), $[D^{2+}]_{aq}^{0.5}$ is the sum of divalent inorganic cations ($Ca^{2+} + Mg^{2+}$) in the aqueous phase (mol/L), and BHS and $D_{0.5}S$ are the organic and inorganic cations, respectively, that are attached to cation exchange sites in the soil (S^-).

The corresponding material balance equations are

$$S_T = [BHS] + [D_{0.5}S] \tag{6}$$

$$D_T = [D^{2+}]_{aq} + 0.5\frac{m}{v}[D_{0.5}S] \tag{7}$$

$$B_T = [B]_{aq} + [BH^+]_{aq} + \frac{m}{v}([B]_s + [BHS]) \tag{8}$$

where S_T (mol/kg) is the total concentration of negatively charged cation-exchange sites equal to the pH-specific cation-exchange capacity (CEC), D_T (mol/L) is the total mass of divalent inorganic cations per aqueous phase volume, B_T (mol/L) is the total mass of the organic amine per aqueous phase volume, and m and v are the soil mass and aqueous-phase volume, respectively.

The TS model (eqs 3−8) contains three chemical components (BH^+(aq), D^{2+}(aq), and $D_{0.5}S$, where protons are not included as a component because pH is known) and seven species (BH^+(aq), B(aq), D^{2+}(aq), $D_{0.5}S$, BHS, B(s), and H^+(aq)), defining component and species according to the conventions outlined by Morel and Hering (*20*). This model was solved by substituting eqs 3−5 into eqs 6−8 resulting in a system of three nonlinear equations evaluating the unknown values of BH^+(aq), D^{2+}(aq), and $D_{0.5}S$ by Newton−Raphson iterations with estimates on K_{oc} and K_G.

Implicit in this model are many assumptions. Interactions with dissolved organic matter are excluded. Any effects due to humic acid−soil mineral interactions (*21*) are ignored. Abiotic or biotic transformations are not considered despite the fact that slow and irreversible formation of covalent bonds between organic amines and specific sites on soil organic matter (i.e., quinones) have been reported in long-term studies (*22, 23*). The last mechanism is excluded because its contribution to mass loss over the first 24 h of exposure is known to be minimal for these soils. No distinction between organic matter, mineral, or amorphous oxide cation-exchange sites is made with respect to their affinities, and all cation-exchange sites are assumed occupied by metal or organic cations. The formation of surface hemisalts (*24*), partitioning of neutral species to conditioned surfaces (*10, 25*), cooperative adsorption (*26*), and complexation reactions (*27*) are ignored. And finally, only calcium and magnesium are considered as exchangeable inorganic cations with equal affinities for exchange sites. The last simplification results from the relative abundance of these cations over other cations in the soil (see Table 2 and ref *28*) and information on their specific affinities to exchangeable sites on other soils (*29*).

Distributed Parameter Model. Solution of the TS model is compatible with the use of $D_{0.5}S$ as a component; however, upon introducing a distributed parameter, selection of an alternative component is required to more appropriately formalize the numerical solution. Following the approach taken by Griffioen (*30*), cation exchange is modeled as two independent processes involving vacant sites (S^-),

TABLE 2. Soil Characteristics

soil	pH^a	sand (%)	silt (%)	clay (%)	OC (%)	CEC^b [cmol (−)/kg] Na$^+$	K$^+$	Mg^{2+}	Ca^{2+}	total
Toronto	4.4	11.9	67.6	20.5	1.34	0.12	0.18	2.75	6.84	9.89
Chalmers	6.5	11.1	72.8	16.0	1.17	0.13	0.16	3.10	9.91	13.3
Drummer	7.2	13.0	66.0	21.2	2.91	0.13	0.57	6.32	20.1	27.1

[a] The pH of a 1 g/mL slurry. [b] Measured at the reported pH.

TABLE 3. Experimental Conditions and SSR for the TS and DP Models

experiments	soil	B_T (mM)	pH[a]	$CaCl_2$ (mM)	m/v (kg/L)	SSR TS model $(mmol/L)^2$	 DP model $(mmol/L)^2$
			Aniline				
1A	Toronto	2.32−0.012	4.04	50	1/5	0.062	0.067
2A	Toronto	0.97−0.007	4.48	5.0	1/5	0.009	0.012
3A	Toronto	1.24−0.008	4.98	0.5	1/5	0.007	0.047
4A	Chalmers	2.63−0.027	6.22	50	1/1	0.276	0.166
5A	Chalmers	1.92−0.020	6.44	5.0	4/3	0.216	0.012
6A	Chalmers	1.81−0.015	6.76	0.5	1/1	0.058	0.058
7A	Drummer	1.84−0.009	6.88	50	1/1	0.607	0.100
8A	Drummer	0.92−0.012	7.16	5.0	1/1	0.044	0.014
totals						1.279	0.476
			α-Naphthylamine				
1N	Toronto	1.46−0.016	4.20	50	1/32	0.031	0.036
2N	Toronto	1.16−0.005	4.49	5.0	1/32	0.009	0.050
3N	Toronto	1.42−0.016	5.08	0.5	1/32	0.022	0.036
4N	Chalmers	1.52−0.016	6.16	50	1/24	0.107	0.027
5N	Chalmers	1.09−0.002	6.56	5	1/24	0.094	0.014
6N	Chalmers	1.19−0.008	6.76	0.5	1/24	0.116	0.006
7N	Drummer	1.28−0.015	6.78	50	1/16	0.042	0.014
8N	Drummer	1.16−0.004	7.43	5.0	1/16	0.054	0.014
totals						0.475	0.197

[a] Average pH of all samples within an experiment.

$$K_{BH} = \frac{[BHS]}{[BH^+]_{aq}[S^-]} \tag{9}$$

$$K_D = \frac{[D_{0.5}S]}{[S^-][D^{2+}]_{aq}^{0.5}} \tag{10}$$

replacing $D_{0.5}S$ with S^- as a component for the system. The new association constants, K_{BH} and K_D for BH^+ and D^{2+}, respectively, are related to K_G by the following expression,

$$K_G = \frac{K_{BH}}{K_D} \tag{11}$$

We represent the frequency distribution as a probability distribution function on log $K_{BH,i}$ allowing for asymmetric (skewed) distributions (*31*),

$$f(x) = \frac{2}{\gamma + \frac{1}{\gamma}} \frac{1}{\sigma\sqrt{2\pi}} \left(e^{-(1/2\sigma^2\gamma^2)(x-\mu)^2}\Big|_{x=\mu}^{x=\infty} + e^{-(\gamma^2/2\sigma^2)(x-\mu)^2}\Big|_{x=-\infty}^{x=\mu}\right) \tag{12}$$

where $f(x)$ is the frequency of sites, $x = \log K_{BH,i}$ with the subscript i denoting the specific site or group of sites having a specific binding coefficient, and μ, σ, and γ represent the mode, standard deviation, and skewness factors, respectively. If $\gamma > 1$, skewness (i.e., the tail) occurs to the right of the mode, and if $\gamma < 1$, skewness is on the left of the mode.

The frequency of sites also is defined by $S_{T,i}/S_T$ where $S_{T,i}$ is the number of sites with a specific log $K_{BH,i}$. The integral of eq 12 over the entire range of possible values of log $K_{BH,i}$ equals unity,

$$\int_a^b f(X)d(X) = 1 \tag{13}$$

where a and b are the lowest and highest values, respectively, of log K_{BH} considered.

This continuous probability distribution describes an infinite number of log $K_{BH,i}$ values. It is reasonable to represent this function with a discrete number of sites, with groups (or compartments) of sites possessing the same value of $K_{BH,i}$. If each compartment contains the same number of sites, discrete expressions for the concentrations of BHS and $D_{0.5}S$ are obtained, again, assuming that the affinity of D^{2+} for all sites is constant,

$$[BHS] = \sum_{i=1}^{i=n}[BHS]_i = [BH^+]_{aq}\sum_{i=1}^{i=n}K_{BH,i}[S^-]_i \tag{14}$$

$$[D_{0.5}S] = \sum_{i=1}^{i=n}[D_{0.5}S]_i = K_D[D^{2+}]_{aq}^{0.5}\sum_{i=1}^{i=n}[S^-]_i \tag{15}$$

where the total number of sites in each compartment is defined by,

$$S_{T,i} = [S^-]_i + K_{BH,i}[BH^+]_{aq}[S^-]_i + K_D[D^{2+}]_{aq}^{0.5}[S^-]_i = \frac{CEC}{n} \tag{16}$$

The value of each log $K_{BH,i}$ corresponding to sites $[S^-]_i$ was found by sectioning the area under the probability function into 600 subareas of equal area, with each log $K_{BH,i}$ equal to the centroid value of subarea i with respect to the $f(\log K_{BH,i})$ axis.

In eqs 14−16, $[S^-]_i$ is the concentration of free sites in compartment i, and $K_{BH,i}$ represents the associated cation-exchange constant corresponding to that specific section. Rearranging eq 16 results in

$$[S^-]_i = \frac{CEC}{n\{1 + K_{BH,i}[BH^+]_{aq} + K_D[D^{2+}]_{aq}^{0.5}\}} \tag{17}$$

Finally, the total concentration of free sites in the soil is expressed as

$$[S^-] = \sum_{i=1}^{i=n}[S^-]_i = \frac{CEC}{n}\sum_{i=1}^{i=n}\frac{1}{\{1 + K_{BH,i}[BH^+] + K_D[D^{2+}]^{0.5}\}} \tag{18}$$

Upon introducing eqs 3, 4, 9, 10, and 18 into the mass balance equations for B_T and D_T (eqs 7 and 8), the following

TABLE 4. Calculated TS and DP Model Parameters [with log (K_D) = 25.0]

	aniline	α-naphthylamine
TS model		
log K_G	0.76	1.94
K_{oc} (L/kg)	30.0	245
DP model		
log μ	23.7	25.1
σ	1.66	2.04
γ	1.00	1.00
K_{oc} (L/kg)	16.5	100

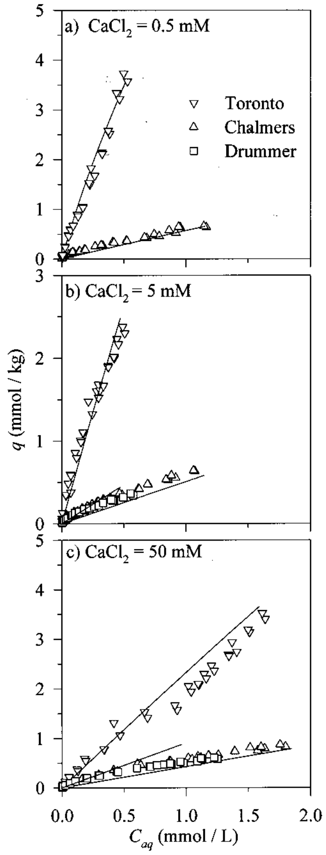

FIGURE 1. Aniline isotherms on Toronto, Chalmers, and Drummer soils measured in (a) 0.5, (b) 5, and (c) 50 mM $CaCl_2$ solutions. Solid lines are TS model predictions. All experimental conditions are provided in Table 3.

pair of nonlinear equations with two unknowns (BH^+ and D^{2+}) is obtained,

$$B_T = [BH^+]_{aq}\left(1 + \frac{K_a}{H^+} + \frac{m}{v}\frac{K_{oc} f_{oc} K_a}{H^+}\right) + [BH^+]_{aq}\frac{CEC}{n}\frac{m}{v}\sum_{i=1}^{i=n}\left(\frac{K_{BH,i}}{1 + K_{BH,i}[BH^+]_{aq} + K_D[D^{2+}]_{aq}^{0.5}}\right) \qquad (19)$$

$$D_T = [D^{2+}]_{aq} + 0.5K_D[D^{2+}]_{aq}^{0.5}\frac{CEC}{n}\frac{m}{v}\sum_{i=1}^{i=n} \times \left(\frac{1}{1 + K_{BH,i}[BH^+]_{aq} + K_D[D^{2+}]_{aq}^{0.5}}\right) \qquad (20)$$

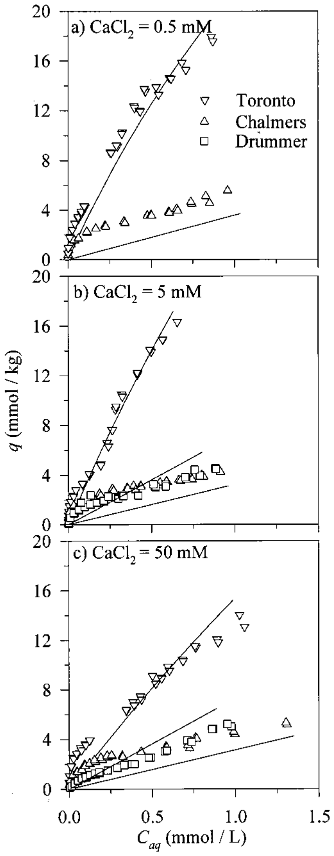

FIGURE 2. α-Naphthylamine isotherms on Toronto, Chalmers, and Drummer soils measured in (a) 0.5, (b) 5, and (c) 50 mM $CaCl_2$ solutions. Solid lines are TS model predictions. All experimental conditions are provided in Table 3.

Because only the relative affinities of D^{2+} and BH^+ for sites are discernible from the experimental data, it is reasonable to make K_D constant over all sites. This choice, rather than choosing a constant K_{BH}, is further justified because adsorption of calcium and magnesium to most sites is dominated by charge−charge attraction, whereas adsorption of an organic amine to specific sites may be greatly influenced by other attractive or repulsive forces. Also, K_D is set to a large value (log K_D = 25) to ensure that the optimum value of K_{BH} is proportionally large, effectively reducing the number of free sites to a negligible value. Equations 12, 19, and 20 are referred to hencefore as a distributed parameter (DP) model with eqs 19 and 20 easily solved by the Newton−Raphson iterative method after descritizing eq 12.

Parameter Estimation and Experimental Methods

Parameter Estimation. For the TS model, the values of K_{oc} and K_G were calculated for the data set by adjusting these values until the global minimum was found for the following objective function,

$$SSR = \sum_{j=1}^{j=n}(C_{aq,m} - C_{aq,p})^2 \qquad (21)$$

where C_{aq} is the total concentration of organic amine in the aqueous phase (=$[BH^+]_{aq}$ + $[B]_{aq}$), the subscripts m and p denote measured and predicted values, respectively, SSR is the sum of squared residuals between experimental and model predictions, and n is the number of data points. The optimum values of K_{oc} and K_G occur at the minimum value of SSR. A similar procedure was followed with the DP model, where K_{oc}, μ, and σ were identified at the global minimum of eq 21, assuming a skewness factor of 1 (=γ) in eq 12.

Experimental Methods. Batch sorption experiments representing mass distributions of aniline or α-naphthyl-

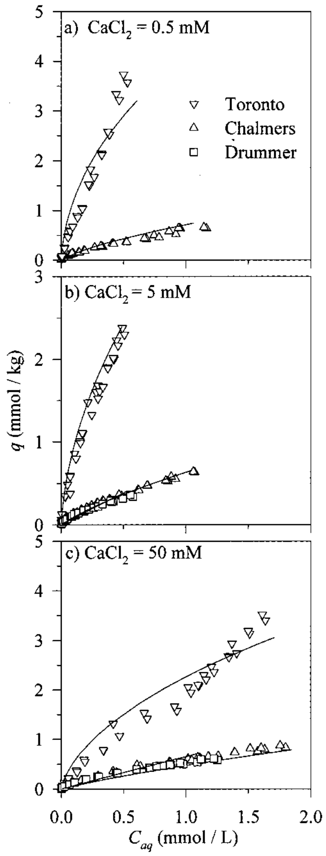

FIGURE 3. Aniline isotherms on Toronto, Chalmers, and Drummer soils measured in (a) 0.5, (b) 5, and (c) 50 mM $CaCl_2$ solutions. Solid lines are DP model predictions with $\gamma = 1$. All experimental conditions are provided in Table 3.

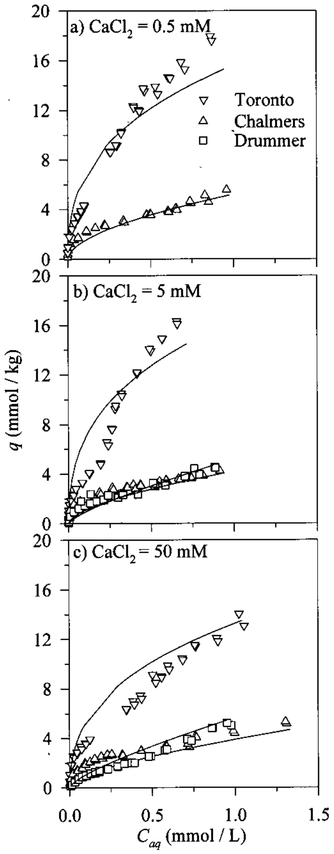

FIGURE 4. α-Naphthylamine isotherms on Toronto, Chalmers, and Drummer soils measured in (a) 0.5, (b) 5, and (c) 50 mM $CaCl_2$ solutions. Solid lines are DP model predictions with $\gamma = 1$. All experimental conditions are provided in Table 3.

amine were measured in three Indiana soils at their natural pH values, at three different ionic strengths, over a range of organic amine concentrations. Some physical and chemical properties of aniline and α-naphthylamine are given in Table 1. Characteristics of the three Indiana soils employed in these studies are shown in Table 2. Toronto is the same soil referred to in Lee et al. (*32*) as Chalmers-4.

Soil samples were hydrated with 0.5, 5, or 50 mM aqueous $CaCl_2$ solutions in 8 mL glass centrifuge tubes outfitted with Teflon-lined screw caps. Tubes were rotated end-over-end for 24 h at 24 ± 3 °C, and centrifuged at 1350*g* for 60 min. Supernatants were sampled for amine analysis, and the pH of the remaining supernatants was measured. Supernatant amine concentrations were measured with a Shimadzu HPLC equipped with a Supelco ABZ or a Supelcosil ABZ+ reversed-phase column, and a UV detector at 254 nm. The mobile phase was an acetonitrile−aqueous acetate buffer (pH = 4.7) with a flow rate of 1.5 mL/min. Soil-sorbed concentrations, *q*, were calculated by difference,

$$q = (v/m)(B_T - C_{aq}) \qquad (22)$$

Peak areas were compared to those of known standards. A more complete methods description is reported elsewhere (*32*).

Results and Discussion

Collecting mass distribution data on three soils at three different ionic strengths over a range of organic amine concentrations for each amine results in variation of the model parameters CEC, $(m/v)f_{oc}$, H^+, D_T, and B_T. For each organic amine, all data (i.e., 276 values for aniline, 292 for α-naphthylamine) were used to find the optimum values of K_{oc} and K_G (TS model) or K_{oc}, μ, and σ (DP model) at the global minimum of eq 21. The data and model results are summarized in Tables 3 and 4 and in Figures 1−4. Table 3 lists experimental conditions for each isotherm, the resulting SSR from each model for each isotherm, and the total value of SSR for each amine. Table 4 reports the optimum values of K_{oc} and K_G for the TS model, and of log μ and σ for the DP model. The lines in Figures 1−4 are calculated at the specific CEC, $(m/v)f_{oc}$, and D_T values and the average pH for the respective isotherm, varying only B_T.

Two-Site Model Results. Figure 1 shows all measured and TS model calculated isotherms for aniline. Experiments with Toronto soil (i.e., pH ∼ 4) resulted in a larger fraction of the aniline residing in the soil phase compared to experiments with the near-neutral pH value soils (Chalmers and Drummer) as expected due to the large fraction of compound existing as the conjugate acid species at low pH. Likewise, increasing $CaCl_2$ concentration resulted in higher concentrations of aniline in all soil solutions, especially for Toronto, the acidic soil. The calculated isotherms indicate that the magnitudes, as well as directions, of these trends are captured by the TS model and associated coefficients. The linearity of the isotherms suggests that the relative affinities of the cation-exchange sites for D^{2+} (Ca^{2+} or Mg^{2+}) and the protonated form of aniline is nearly constant, consistent with previous observations (*18, 26*). Because the amines were added to the soil slurries at concentrations below the CEC, the model predicts a significant fraction of sites are occupied by Ca^{2+} and Mg^{2+} due to mass balance constraints.

The meaured and TS model calculated isotherms for α-naphthylamine are provided in Figure 2. Again, the general pH and ionic strength trends in the data are consistent with model predictions. The calculated value of log K_G is greater

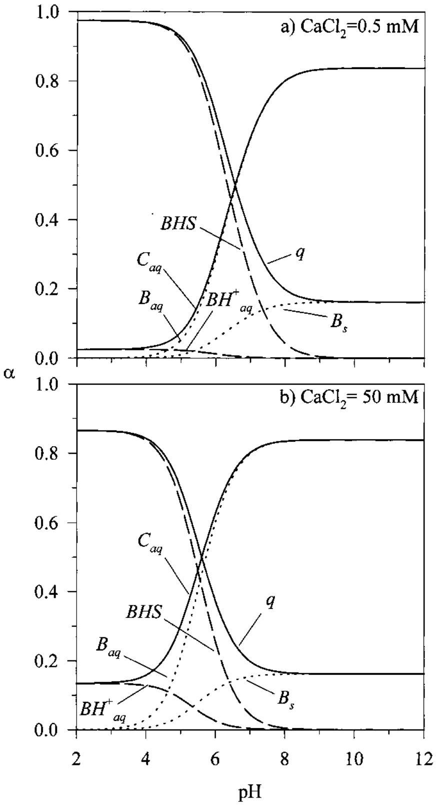

FIGURE 5. Aniline speciation as a function of pH in Chalmers with (a) 0.5 and (b) 50 mM CaCl$_2$ calculated with the DP model with log μ = 24.34 and σ = 1.38, and B_T = 1.6 mmol/L. All concentrations are expressed as fractional values (α = [species]/B_T).

for α-naphthylamine than for aniline, and both values are positive, indicating that these organic cations have in general higher affinities for the cation-exchange sites than the inorganic cations (*24, 32*) and that selectivity increases with hydrophobicity (*24*). However, the calculated isotherms do not capture the nonlinear trends displayed by the experimental isotherms.

Distributed Parameter Model Results. The data in Figures 1 and 2 is shown also in Figures 3 and 4 with DP model calculated isotherms. Again, the optimum values of K_{oc}, log μ, and σ used to construct the calculated isotherms are provided in Table 4. The magnitude of log μ is relative to the value assigned to log K_D and can be compared to log K_G by subtracting log K_D from log μ. For the individual isotherms, the DP model with global optimum values of K_{oc}, log μ, and σ provided better or similar results as those predicted by the TS model, based on the SSR values.

The values of K_{oc}, calculated for each compound with each model, can be compared to values estimated by the regression presented by Sabljic et al. (*33*) for the neutral form of anilinium compounds (n = 20, r = 0.91),

$$\log K_{oc} = 0.85 + 0.62 \log K_{ow} \qquad (23)$$

of 25.7 and 174 L/kg for aniline and α-naphthylamine, based on K_{ow} values of 8 and 175, respectively (*32*). The optimum values of K_{oc} found for both the ST and DP models are within a factor of 2 of these values.

The σ parameter is larger for α-naphthylamine than for aniline as expected as this parameter is a good indicator of isotherm nonlinearity. The larger values for α-naphthylamine result in a wider range of log K_{BH} values. The larger values of log K_{BH} are partially offset by a reduced μ/K_D (= K_G) ratio compared to the singular value of K_G calculated with

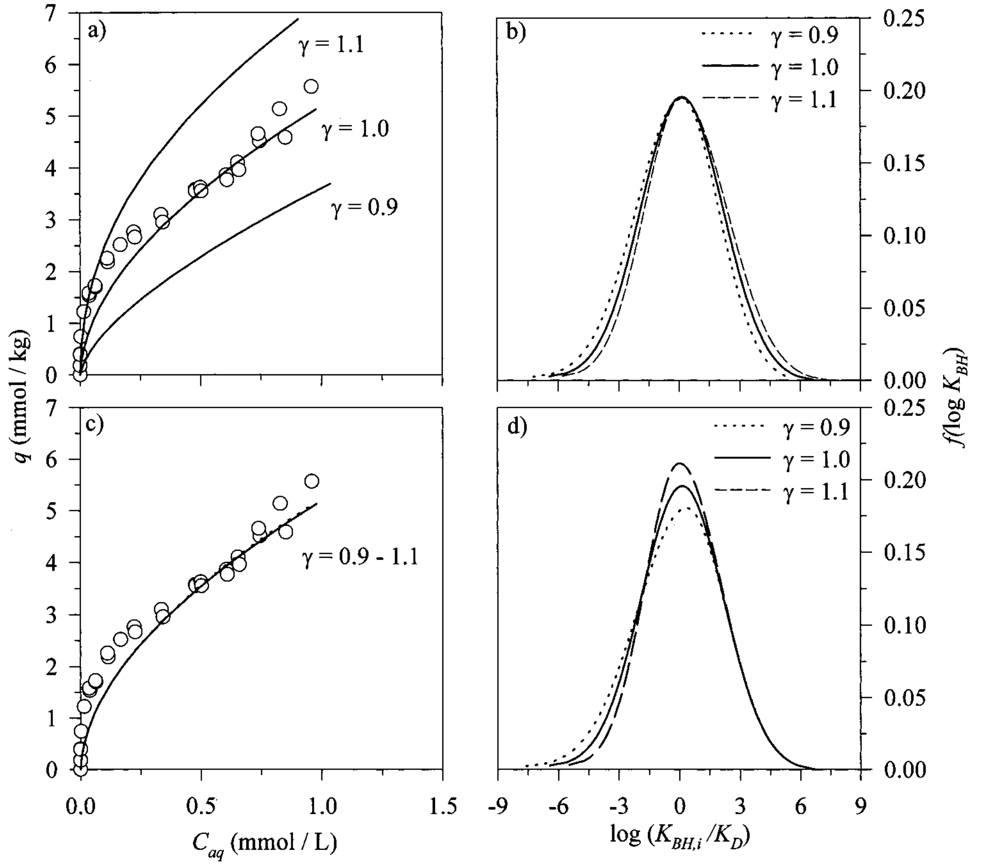

FIGURE 6. α-Naphthylamine isotherms in Chalmers soil with 0.5 mM CaCl$_2$ (panels a and c) and the corresponding frequency distributions (panels b and d).

the TS model. The unimportance of lower log K_{BH} values will become apparent in the subsequent discussion regarding skewness.

The soil mineral portion of our soils is mainly montmorillonite clay, and the organic contents of these soils do not vary widely. These facts surely contribute to the goodness of fit found with the singular values for K_G, log μ, and σ for each compound with these soils. Optimum values of these same parameters clearly may differ among widely varying soil types, and specifically for soils composed primarily of other clay type (i.e., vermicullite, kaolinite).

Calculated Speciation. The TS and DP models are based on chemical speciation and phase-transfer processes of species; however, the coupled impact of these processes is not explicitly conveyed in Figures 1−4. In Figure 5, therefore, we present two cases of calculated speciation as a function of pH. The cases are 1.6 mM aniline in Chalmers soil with 0.5 or 50 mM added $CaCl_2$, $m/v = 1$, and the reported CEC measured at pH 6.5. At pH 6.5, the major species of aniline in a 0.5 mM $CaCl_2$ slurry are calculated to be B_{aq}, BHS, and B_s at approximate proportions of 45:45:10. In a 50 mM $CaCl_2$ slurry, the distribution of these major species is approximately 75:12:13. In both cases, a significant amount of aniline on the soil is calculated to exist as the protonated species despite the negligible contribution of the aqueous phase protonated species to aniline's total mass balance.

Skewness. A normal probability distribution function on log $K_{BH,i}$, is a skewed distribution on $K_{BH,i}$ due to the logarithmic transformation. Therefore, the effect of additional skewing on the probability distribution was examined. Distributions on log($K_{BH,i}/K_D$) at $\gamma = 0.9$, 1.0, and 1.1 are shown in Figure 6b, employing the values of μ and σ previously calculated for α-naphthylamine listed in Table 4. The measured and calculated isotherms, corresponding to these distributions, are shown in Figure 6a for α-naphthylamine in Chalmers soil with 0.5 mM $CaCl_2$. For $\gamma = 1.1$, the distribution is skewed to higher affinity sites, resulting in a greater isotherm slope at low B_T and an increased soil-phase amine concentration at all values of B_T. Opposite trends are seen for $\gamma = 0.9$.

Whether or not a suitable set of $\mu - \sigma$ values could be found at $\gamma \neq 1$ was evaluated. For this purpose, optimum values for log μ and σ at two values of $\gamma \neq 1$ were found for all α-naphthylamine data with log K_{oc} set equal to the previously calculated value (=2). Log μ and σ values of 25.4 and 2.20 and 25.0 and 1.88, respectively, for $\gamma = 0.9$ and 1.1 were calculated. The corresponding isotherms for Chalmers soil with 0.5 mM $CaCl_2$ for $\gamma = 0.9$, 1.0, and 1.1 are shown in Figure 6c, with the corresponding distributions of log($K_{BH,i}/K_D$) shown in Figure 6d. Clearly, all three parameter sets result in nearly identical isotherms for this case, and this is true for all other conditions. Figure 6d indicates that even though the frequency distributions are quite different over the low-affinity sites, they provide the same distribution for the high-affinity sites. It may be concluded that description of the affinities of high affinity sites ($K_{BH,i} > \mu$) is most important for isotherm construction. From a physical standpoint, we interpret this to arise from these soils having exchangeable sites that may be groups into two general categories: (1) sites where specific electrical (e.g., inner-sphere complexes) or nonspecific electrochemical (e.g., adsorption through hydrophobic and ionic interactions) interactions occurs, and (2) sites where nonspecific electrical association occurs (e.g., association through hydration spheres). The first type would lead to preferential surface complexation of specific cations, whereas the second would result largely in the preferential adsorption of divalent cations over most monovalent cations due to electrical charge effects. Distributed association constants merge these extreme classifications into a continuum that is likely more descriptive of natural soil heterogenity.

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