

Quinoline Sorption on Kaolinite–Humic Acid Complexes

Jon Chorover,* Mary Kay Amistadi, William D. Burgos, and Patrick G. Hatcher

ABSTRACT

Adsorption of quinoline ($pK_a = 4.92$) and background electrolyte (LiCl) onto specimen kaolinite was measured as a function of surface-bound humic acid (HA) concentration ($f_{oc} = 0\text{--}0.5\%$), pH (3–10), and ionic strength (1–10 mM). Complexation of HA on the kaolinite surface (4.5 mg C kg^{-1}) reduced the point of zero net charge (pzc) for kaolinite by more than one pH unit and resulted in a significant increase in negative surface charge. Maximum sorption of quinoline occurred near its pK_a for all sorbents. Below the pK_a , quinoline sorption increases with increasing pH and decreasing proton competition. Above the pK_a , sorption is reduced in parallel with (but offset to a higher pH from) the ionized fraction. Competition with Li^+ for surface sites is apparent from diminished quinoline adsorption with increasing ionic strength, but sorption of the ionized form of quinoline is always favored and kaolinite exhibits selectivity for cationic quinoline over Li^+ ($K_{exc} = 65$ at pH 5). However, increasing f_{oc} diminishes quinoline sorption and selectivity ($K_{exc} = 32$ at pH 5) and increases sorption reversibility relative to uncoated kaolinite. Humic acid alone exhibits lower selectivity for quinoline ($K_{exc} = 4$ at pH 5). The results indicate that mineral-sorbed humic substances can diminish retention of cationic quinoline despite an increase in overall cation-exchange capacity.

RETENTION in soil of nonpolar polycyclic aromatic compounds (PACs) results primarily from interaction with solid-phase humic matter. Sorption has often been correlated with the mass fraction of soil organic C (f_{oc}) and sorbate hydrophobicity [e.g., the octanol-water partition coefficient, K_{ow}] (Means et al., 1980; Hassett et al., 1981; Chiou, 1989; Wershaw, 1991; Schwarzenbach et al., 1993). Most mineral surfaces weakly adsorb low quantities of nonpolar PACs (Schwarzenbach and Westall, 1981; Karickhoff, 1984; Zhang et al., 1990), and sorption increases with the amount of mineral-bound organic matter (Murphy et al., 1994). For nonpolar compounds, variation in the sorbed quantity of nonionic PAC with pH and ionic strength has been attributed to conformational variability of humic substances (Schlautman and Morgan, 1993).

A broad group of environmental contaminants termed *ionizable* PACs includes the N heterocyclic compounds (NHCs), whose weakly basic N heteroatom is protonated to cationic form in the acidic pH range of natural waters (Southworth and Keller, 1984; Zachara et al., 1987). The few studies that have been conducted to date indicate that NHC (e.g., quinoline) sorption on soils (Zachara et al., 1986, 1987) and humic substances (Nielsen et al., 1997) is affected significantly by solution

pH and compound ionization. In contrast to the case for neutral PACs, an equilibrium partition model, whereby NHCs sorb in direct proportion to f_{oc} , is not supported by the available data. Retention of cationic NHCs may be strongly dependent on the nature and density of anionic surface functional groups associated with soil clays and native organic matter, but prior studies have not included measurements of soil surface composition and its variation with solution chemistry. Competition with background electrolyte for cation sorption sites may also be a factor. As a result, soil selectivity for cationic NHCs vs. inorganic cations will probably affect contaminant fate.

The role of mineral-bound humic substances in NHC sorption is unknown. Bound humic materials may influence mineral sorbent affinity by altering the type and charge of surface functional groups (Davis, 1982; Kretzschmar et al., 1997) or by altering the relative predominance of hydrophobic sorption sites (Schlautman and Morgan, 1993). Whereas the former effect may be significant for the ionized compound, the latter is more likely to influence retention of the neutral species. Prior work has indicated that cation exchange of ionized quinoline is important in its adsorption to subsurface material at acid pH (Zachara et al., 1986; 1987; Ainsworth et al., 1987). Hence, if sorption of humic substances to kaolinite increases the net negative charge of the surface, affinity for adsorption of cationic NHCs may be likewise affected. Further work is needed to identify the relative importance of mineral vs. organic soil constituents to NHC sorption as a function of solution chemistry. The objective of our study was to examine the effects of mineral-bound humic substances on the sorption of the NHC quinoline (C_9H_7N , $pK_a = 4.94$) to kaolinite across the pH range encountered in natural soils and water.

MATERIALS AND METHODS

Preparation of Electrolyte-Saturated Kaolinite

All solutions were prepared using distilled water that was passed through a MilliQ UV-plus water purification system. Poorly crystallized Georgia kaolinite (KGa-2) was acquired from the Source Clay Minerals Repository and 250 g were added slowly to 1 L of MilliQ H_2O while stirring. The kaolinite was dispersed for size fractionation by adjusting suspension pH to 9.5 with dropwise addition of LiOH. The suspension was size fractionated by centrifugation, and particles with equivalent settling diameters $>2 \mu\text{m}$ were discarded. The suspension was flocculated by addition of concentrated LiCl solu-

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Abbreviations: BET, Brunauer–Emmett–Teller; CPMAS-NMR, cross-polarization magic angle spinning nuclear magnetic resonance spectroscopy; DOC, dissolved organic C; EGME, ethylene glycol monoethyl ether; f_{oc} , mass fraction of soil organic C; HA, humic acid; NHC, N heterocyclic compound; PAC, polycyclic aromatic compound; pzc, point of zero net charge; TOC, total organic C.

tion and HCl to give a suspension concentration of 1.0 mol kg⁻¹ LiCl and pH 3. The suspension was shaken for 20 min and then centrifuged in 250 mL of polypropylene copolymer bottles for 10 min at 6000 g. Supernatant solutions were discarded. The kaolinite was resuspended in 225 g of 1.0 M LiCl solution (pH 3), shaken for 20 min and centrifuged, with the procedure repeated until the supernatant solution reached pH 3. Clay was resuspended in 225 g of 0.01 M LiCl and washed five more times to raise supernatant solution pH to 5.5. The clay was finally redispersed in 0.01 M LiCl and the solid concentration of the stock suspension was measured by oven drying quadruplicate samples to constant mass, correcting for the contribution of LiCl. Specific surface area of the kaolinite was measured by N₂ (gas) Brunauer–Emmett–Teller (BET) and ethylene glycol monoethyl ether (EGME) methods. Structural (permanent) charge was measured by Cs adsorption (Anderson and Sposito, 1991). Selected characterization data are presented in Table 1.

Extraction, Purification and Characterization of Humic Acid

Humic acid was extracted from the A horizon of a northern hardwood Typic Dystrichrept forest soil collected from Nittany Ridge, Centre County, PA. Extraction of the Nittany Ridge HA in NaOH under N₂ (gas) and purification in HF–HCl were performed using standard procedures (Swift, 1996). Following acid treatment, HA was dialyzed (SpectraPor 3500 MWCO, Spectrum Laboratories, Laguna Hills, CA) against MilliQ H₂O until Cl⁻ was not detected in the dialysate. Ash content was <2%. The HA was freeze-dried prior to use. Carbon content of the HA was measured on a Shimadzu TOC 5000A (Shimadzu Scientific Instruments, Columbia, MD) equipped with a solid-sample module, and structural group content was measured by ¹³C cross-polarization magic angle spinning nuclear magnetic resonance spectroscopy (CPMAS-NMR). Carboxylic and phenolic group acidity were measured using a modification of the alkalimetric titration method of Bowles et al. (1989). Characterization data are presented in Table 1.

Kaolinite–Humic Acid Complexes

Kaolinite–humic acid complexes were prepared by reacting kaolinite with HA at pH 4.5 in 0.01 M LiCl, followed by repeated washing in HA-free LiCl solution to remove the easily desorbable fraction. Stock HA suspensions were prepared by dissolving 0.1 g of HA in 0.10 kg of MilliQ H₂O in an acid-washed amber glass vessel maintained at pH 7 for 24 h. The dissolved organic C (DOC) concentration of the stock suspension was measured with a Shimadzu TOC 5000A analyzer. Five hundred grams of 0.01 M LiCl were added to a weighed and tared glass flask containing a magnetic stir bar. Stock HA was added to give total organic C (TOC) concentrations in the final suspension equal to ≈25, 50, or 110

mg kg⁻¹ while stirring. The pH was adjusted to pH 4.5 by addition of 0.1 M HCl and equilibrated until a stable pH reading was achieved. Ten grams (oven-dry equivalent) LiCl-saturated kaolinite were then added as a suspension to the contents of the flask while stirring vigorously. Total suspension mass was increased to 1.000 kg at pH 4.5 by addition of 0.01 M LiCl and 0.01 M HCl. The suspension was stirred gently at 25°C and maintained at pH 4.5 in the dark for 24 h.

Contents of the flask were transferred quantitatively into preweighed 250-mL polypropylene copolymer centrifuge bottles and centrifuged at 15 000 g for 20 min. Supernatant solution was aspirated into glass containers and stored for equilibrium DOC measurement. Complexes were resuspended in 200 g of 1.0 mM LiCl solution preset to pH 5 and reacted by gentle rotation at 7 revolutions per minute for 4 h. Suspensions were centrifuged and supernatant solutions were aspirated into glass containers and stored for DOC measurement (Wash 1). This step was repeated two more times (Wash 2 and Wash 3). The amount of HA C sorbed to the kaolinite (*f*_{OC}) was calculated from

$$f_{OC} = ([TOC]_{initial} - [DOC]_{eq})M_{TW, susp} - (\sum [DOC]_{wash x})M_{TW, wash x} \quad [1]$$

where [TOC]_{initial}, [DOC]_{eq}, and [DOC]_{wash x} are the C concentrations (mg kg⁻¹) in the initial suspension (total), the supernatant solution after the 24-h equilibration, and the supernatant solution corresponding with *x* desorption washes, respectively, and *M*_{TW} is the gravimetric water content of the suspension or wash (kg of solution per kg of kaolinite). The first term in Eq. [1] gives the amount of organic C retained on the kaolinite surface during the adsorption process and the remaining *x* terms correspond with the amount of organic C removed during subsequent *x* washing steps. Values of *f*_{OC} are reported in percentage of C. Stock kaolinite–humic acid suspensions were stored in amber vials at 2°C prior to use. The solid concentration of each stock suspension was measured by oven drying quadruplicate samples to constant mass.

Quinoline Sorption Experiments

Reagent grade quinoline (99%) was purchased from Aldrich Chemical (Milwaukee, WI) and used without further purification. Quinoline was dissolved in LiCl at the desired ionic strength to produce a stock concentration of 4.1 mmol L⁻¹. Sorption of quinoline onto kaolinite and humic-coated kaolinite was measured as a function of pH at 16 duplicated pH values [pH 3–10] and two ionic strengths [1.0 and 10.0 mmol kg⁻¹ LiCl]. For each batch system, 200 mg of kaolinite or kaolinite–humic complex were added to 50-mL teflon centrifuge tubes of known mass. Variable proportions of either 1.0 or 10.0 mmol kg⁻¹ LiCl and HCl or LiOH solutions were added to each tube to give the desired range in equilibrium pH values. Quinoline stock solution was then added to each tube to give a total quinoline concentration of 0.1 mmol kg⁻¹

Table 1. Selected physical and chemical characteristics of adsorbents used in the study.

Assignment	Nittany Ridge humic acid (54.8% C)				Kaolinite (KGa-2)				
	CPMAS ¹³ C NMR data summary†				Functional group acidity		Specific surface area‡		
	Alkyl	O-Alkyl	Aromatic	Carbonyl	Carboxylic	Phenolic	EGME	N ₂ BET	Structural charge (σ _a)
Chemical shift % of Total C	0–65 ppm 35	65–100 ppm 12	100–160 ppm 32	160–200 ppm 21	— mol _c kg ⁻¹ C —		— m ² g ⁻¹ —		mmol _c kg ⁻¹
					5.18	2.48	19.1	23.2	-13.4 ± 0.2

† CPMAS-NMR is cross-polarization magic angle spinning nuclear magnetic resonance spectroscopy.

‡ EGME is ethylene glycol monoethyl ether; BET is Brunauer–Emmett–Teller.

and a total suspension mass of 41.0 g. Blanks were prepared as outlined above, but without kaolinite. Centrifuge tubes were closed with teflon sealing caps and suspensions were equilibrated by end-over-end rotation at 7 revolutions per minute and 25°C for 24 h.

Following equilibration, suspensions were centrifuged at 27 000 *g* and 25°C for 20 min. Supernatant solutions were aspirated into glass vials and final proton concentration was measured immediately using an Orion 8401 combination glass electrode (Orion, Boston, MA) calibrated by Gran titration at the experimental ionic strength (Chorover and Sposito, 1995). The supernatant solution was then acidified to pH 2 by addition of HNO₃ and stored at 2°C prior to analysis. The mass of solution entrained in the humic–clay slurry was measured. Clay–humic complexes were then extracted with 20 g of 0.1 mol kg⁻¹ NH₄NO₃ on a reciprocal shaker for 30 min, and this procedure was repeated three times. Extraction solutions for each sample were combined into one container, and total mass was determined. Solution was acidified and stored at 2°C prior to analysis.

Quinoline concentration in the supernatant and extracting solutions was measured by high performance liquid chromatography on a reverse-phase (Beta-Basic 18, Keystone Scientific, State College, PA) column, followed by UV (315 nm) detection (HPLC, Waters Inc., Milford, MA) equipped with a Shimadzu variable wavelength detector) within 24 h. The mobile phase consisted of 30% (v/v) acetonitrile in 50 mM triethylamine-phosphate buffer at pH 3.5. Dissolved organic C concentrations in the supernatant solution (corrected for quinoline concentration) were measured to confirm that negligible HA desorption occurred during the experiment. Concentration of background electrolyte in supernatant and extraction solutions was measured by atomic emission spectrometry for Li⁺ (I.L. Video 22, Thermo Jarrell Ash, Franklin, MA) and ion chromatography for Cl⁻ (DX-500, Dionex Corp., Sunnyvale, CA).

The surface excesses of Li⁺ and Cl⁻ were calculated from the concentrations and solution masses measured:

$$q_i = N_{i, \text{NH}_4\text{NO}_3} - M_{\text{ent}} m_i \quad [2]$$

where q_i is the surface excess of Li or Cl (moles per kilogram of adsorbent), $N_{i, \text{NH}_4\text{NO}_3}$ is the number of moles per unit clay mass of Li or Cl extracted in the NH₄NO₃ step, M_{ent} is the mass of entrained solution per unit clay mass, and m_i is the molinity (moles per kilogram of solution) of Li or Cl in the supernatant solution. The quantity of quinoline sorbed (Γ_Q) was calculated on the basis of loss from solution and accounts for any loss (found to be negligible) to the reactor vessel:

$$\Gamma_Q = (m_{Q,0} - m_{Q,\text{eq}}) M_W \quad [3]$$

where $m_{Q,0}$ and $m_{Q,\text{eq}}$ are, respectively, the molinities of quinoline in the supernatant solution of a sorbent-free blank and the experimental suspension following 24-h equilibration time, and M_W is the total mass of solution per unit solid mass (kg solution per kg solid).

Calculation of Intrinsic Surface Charge Density

The effect of humic sorption and pH on kaolinite surface charge was calculated directly on the basis of ion adsorption. The intrinsic surface charge density (σ_{in}), which is the sum of structural (resulting from isomorphous substitutions) and net proton charge densities, is balanced by adsorption of ions other than H⁺ and OH⁻ (Sposito, 1992). Therefore, measured values of surface excess for background electrolyte (Li⁺ and Cl⁻) and the protonated form of quinoline (QH⁺) were used

to calculate σ_{in} from the relation $\sigma_{\text{in}} = -\Delta q$, where Δq is the difference between net adsorbed cation and anion charge densities. Net proton surface charge density, σ_{H} , is readily calculated from $\sigma_{\text{H}} = \sigma_{\text{in}} - \sigma_{\text{O}}$, where σ_{O} is the structural charge density given in Table 1.

Quinoline Sorption to Humic Acid

The sorption of quinoline to HA in the absence of kaolinite was measured radiochemically at two ionic strengths (1.0 and 10.0 mmol kg⁻¹ LiCl) across the pH range 3 to 9. Quinoline stock solution was prepared from reagent grade quinoline and ¹⁴C-quinoline (specific activity = 46.5 mCi mmol⁻¹, Chemsyn Science Laboratories, Lenexa, KS) to give a 2.7 mM solution with 20% of total quinoline ¹⁴C-labeled. Variable proportions of either 1.0 or 10.0 mmol kg⁻¹ LiCl and HCl or LiOH were added to amber glass jars (250 mL) fitted with teflon-lined lids. Aliquots of the solutions were transferred into dialysis bags (SpectraPor 6, 1000 MWCO, 25 cm length, Spectrum Laboratories) and HA stock added to give a final concentration of 65 mg DOC kg⁻¹ in 30 g internal suspension. Total suspension mass was 225 g. Blanks were prepared as above, at pH 4 and pH 7 with no HA added to the internal solution. The bags were clamped and submerged into the reaction jars. Aliquots (200 μ L) of the quinoline stock were then added to the external solutions to give a total system quinoline concentration of 2.4 μ mol kg⁻¹, providing the same ratio of quinoline to total sorbent as in the kaolinite experiments. Reaction vessels were sealed and placed on an oscillating shaker (60 revolutions per minute). Suspensions were equilibrated for 69 h at 25°C. The internal and external solutions were analyzed as above for H⁺, Li⁺, and Cl⁻ concentrations. Corresponding quinoline concentrations were determined by liquid scintillation counting (Beckman LS8100, Beckman Instruments, Waldwick, NJ). Sorption of quinoline and electrolyte to HA was calculated from the difference between internal and external analyte concentration, normalized to HA concentration in the internal suspension.

RESULTS AND DISCUSSION

Sorption of Humic Acid to Kaolinite

Figure 1 shows the effect of equilibrium DOC concentration, [DOC]_{eq}, on the quantity of HA adsorbed to kaolinite at pH 4.5. The steep initial slope of the adsorption isotherm (filled symbols) indicates an increase in high affinity adsorption with increasing [DOC]_{eq} from 0 to 3 mg L⁻¹. However, further increases in DOC do not result in increased adsorption; maximum retention of HA on the kaolinite surface is ≈ 4.8 g C kg⁻¹. Similar values for HA adsorption maxima on KGa-2 have been reported by Kretzschmar et al. (1997). In comparison to the amount sorbed, relatively small quantities of HA were desorbed during the three washing steps in DOC-free 10 mM LiCl, pH 4.5 solution. After removing this easily desorbed fraction of HA, stock kaolinite and kaolinite–humic complexes comprising organic C fractions (f_{OC}) of 0, 0.23, and 0.43% were used in quinoline adsorption experiments.

Intrinsic Surface Charge Density

The effect of HA sorption on the intrinsic surface charge density of kaolinite is shown in Fig. 2. Surface charge decreases with increasing pH in all cases, but

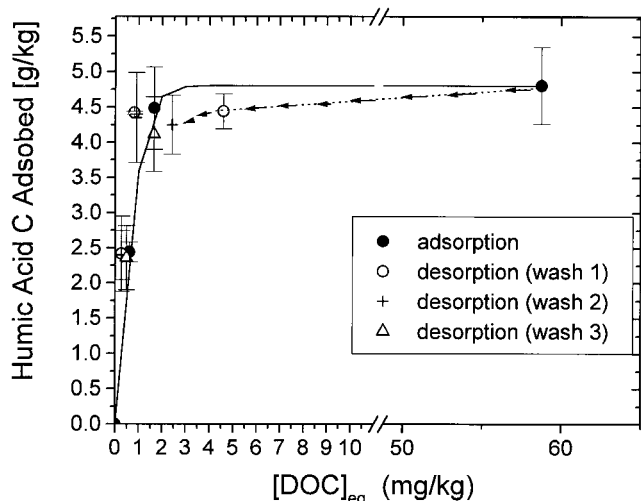
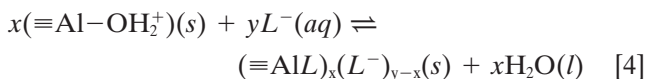


Fig. 1. Adsorption-desorption isotherm for Nittany Ridge humic acid on kaolinite (pH = 4.5, 25°C). Filled symbols represent adsorption and open symbols indicate the amount of surface HA retained at a given equilibrium dissolved organic C (DOC) concentration after one, two, or three washes in (initially) DOC-free LiCl solution.

the magnitude of σ_{in} at any pH depends on f_{oc} and ionic strength. The point of zero net charge (pzc, $\sigma_{in} = 0$) decreases with increasing ionic strength and increasing f_{oc} . High humic coverage ($f_{oc} = 0.43\%$) increases net negative surface charge relative to uncoated kaolinite regardless of ionic strength. However, at intermediate f_{oc} (0.23%), σ_{in} is invariant with ionic strength and, thus, exhibits less negative surface charge than uncoated kaolinite at pH > 4.5.

The effects of f_{oc} on σ_{in} can be interpreted on the basis of HA functional group chemistry and sorptive interactions. An upper limit for the contribution of HA to negative surface charge can be calculated from the carboxylic and phenolic contents of the HA (Table 1) and the measured f_{oc} values. Total concentrations of carboxylic functional groups in the kaolinite-humic complexes are 12 and 23 $\text{mmol}_c \text{kg}^{-1}$ for f_{oc} values of 0.23 and 0.43%, respectively. Phenolic hydroxyls contribute a maximum of 7 and 13 $\text{mmol}_c \text{kg}^{-1}$ to surface proton dissociation at pH > 7. A portion of the acidic functional groups are involved in binding HA to aluminol groups at the kaolinite surface via ligand exchange reactions (Davis, 1982) and, therefore, will not contribute to negative surface charge. This reaction may be written schematically to examine effects on surface charge:



where x protonated aluminol groups react with an HA molecule, represented here as a polyelectrolytic anion comprising y dissociated functional groups, L^- (carboxylate, phenolate). The ligand exchange reaction results in the coordination of x humic functional groups with surface Al atoms, leaving a portion, $(L^-)_{y-x}$, available for subsequent sorption reactions involving protons and other cations (Li^+ and protonated quinoline). At low surface coverage of HA, the relative concentration of

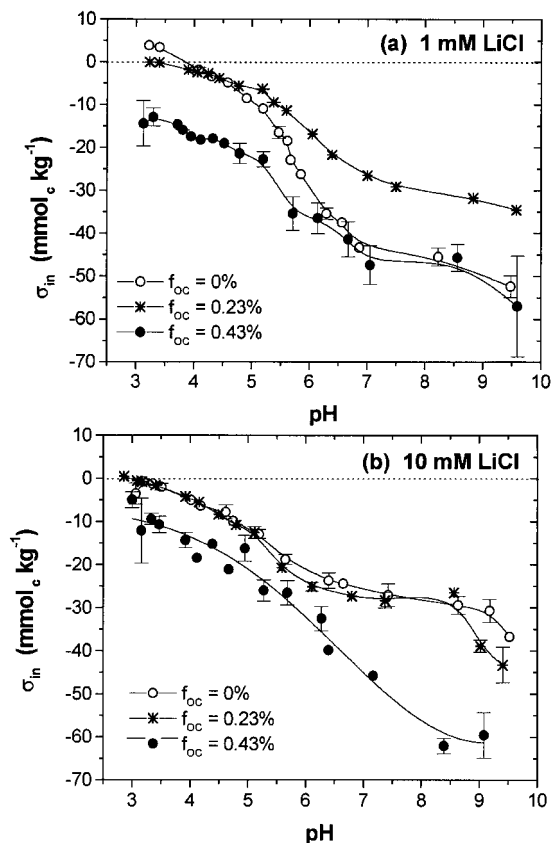


Fig. 2. Intrinsic surface charge density (σ_{in}) as a function of pH and f_{oc} at 25°C: (a) 1 mM LiCl, (b) 10 mM LiCl.

dissociated humic functional groups may be low as a result of surface interaction. Our results are consistent with this reaction if, at low f_{oc} , $y - x$ is small and sorption of HA decreases aluminol positive charge at low pH and negative charge at high pH (Fig. 2a). At maximum sorption of HA ($f_{oc} = 0.43\%$), $y - x$ is larger, consistent with an observed increase in negative surface charge (Fig. 2).

For uncoated kaolinite, σ_{in} in 1 mM LiCl solution decreases from 2.5 to $-50 \text{ mmol}_c \text{kg}^{-1}$ as pH is increased from 3.5 to 9.0 (Fig. 2). This change in σ_{in} , which is a direct measure of proton dissociation from kaolinite surface groups, hereafter referred to as “ $\Delta\sigma_{in}$ (pH 3.5–9.0)”, decreases from 53 to 34 $\text{mmol}_c \text{kg}^{-1}$ with increasing ionic strength from 1 to 10 mM LiCl. These results are in agreement with those calculated from proton adsorption data (Carroll-Webb and Walther, 1988) that show a decrease in $\Delta\sigma_{in}$ (pH 4–8) with increasing ionic strength from 1 to 10 mM NaNO_3 . This trend with ionic strength is in contrast to that reported for simple oxides, which generally show increased $\Delta\sigma_{in}$ with increasing electrolyte concentration (Stumm and Morgan, 1996). Model calculations by Kraepiel et al. (1998) suggest that this difference in acid-base behavior between oxides and layer-type silicates may be attributed to the presence of structural charge in the latter (Table 1) and its net effect on proton adsorption.

Adsorption of HA progressively reverses the effect of ionic strength on surface charge. For $f_{oc} = 0.23\%$,

$\Delta\sigma_{in}$ (pH 3.5–9.0) is largely unaffected by ionic strength (I) (34 mmol_c kg⁻¹ for $I = 1.0$ mM and 36 mmol_c kg⁻¹ for $I = 10$ mM) but an increase in $\Delta\sigma_{in}$ (pH 3.5–9.0) from 36 to 52 mmol_c kg⁻¹ with increasing ionic strength is measured for the highest f_{oc} (0.43%). Increased acidity (dissociation) with increasing ionic strength has been observed in numerous prior potentiometric studies of HA (e.g., Barak and Chen, 1992; Stevenson, 1994) and kaolinitic soils with native f_{oc} values >1% (Chorover and Sposito, 1995). Values of σ_H (net adsorbed proton charge) follow the exact trends shown in Fig. 2 except that all curves are shifted upward by a constant value (13.4 mmol kg⁻¹) equal to $-\sigma_0$.

Prior research has shown that the rate of Al and Si release from kaolinite increases with surface protonation below pH 6 (Carroll-Webb and Walther, 1988; Wieland and Stumm, 1992). Hence, at low pH, adsorbed protons are consumed in mineral dissolution and replaced with adsorbed Al. Surface Al also competes with index cation (Li⁺) for adsorption sites and this is reflected in a progressive increase in the pznc with increased equilibration time (Schroth and Sposito, 1997). Although a 24-h equilibration time was used consistently in our study, the effects of sorbed HA on the rate of kaolinite dissolution and the readsorption of Al are not known.

Quinoline Sorption to Kaolinite–Humic Complexes

Figure 3 shows the effects of ionic strength, f_{oc} , and pH on quinoline sorption. The dotted line represents α , the ionized (protonated) fraction of quinoline — the *quinolinium ion* — in solution. The value of α is given by $[QH^+]/[Q]_T$, where $[QH^+]$ and $[Q]_T$ represent the concentrations of ionized and total quinoline, respectively. The ionized fraction is calculated from the measured proton concentration and the acid dissociation constant for quinoline ($pK_a = 4.92$). Activity coefficients for H⁺ and QH⁺ are determined from the Davies equation, and the neutral species is assigned an activity coefficient of unity (Stumm and Morgan, 1996). Note that *values* on the ordinate correspond with total sorbed quantities and not with the ionized fraction; the latter, which is a unitless quantity that approaches 1.0 at pH < 2 and zero at pH > 8, is shown as an overlay on each graph for reference.

The pH-dependent qualitative trends are independent of f_{oc} and ionic strength: at low pH, sorption increases with increasing pH to a maximum (Γ_{max}) at pH $\approx pK_a$, and then decreases in parallel with ionized quinoline at pH > pK_a . However, increasing either ionic strength or f_{oc} has a negative impact on quinoline sorption. (Note the difference in y-axis scales in Fig. 3a and 3b.) For f_{oc} values of 0 and 0.43%, the tenfold increase in ionic strength resulted in 36 and 47% reductions in Γ_{max} , respectively. In a manner similar to the patterns for surface charge, at intermediate f_{oc} , changes in ionic strength had no detectable effect on Γ_{max} .

Evidently, the quinolinium ion is sorbed to kaolinite and kaolinite–humic sorbents to a greater extent than

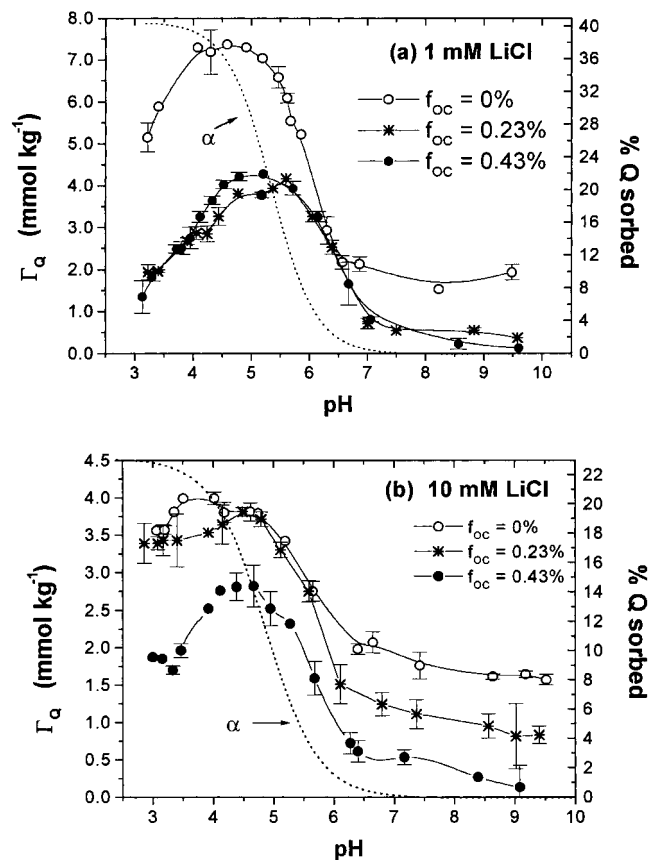


Fig. 3. Quinoline sorption as a function of pH and f_{oc} at 25°C: (a) 1 mM LiCl, (b) 10 mM LiCl. The dotted line represents the ionized fraction in solution ($[QH^+]/[Q]_T$) which decreases from ≈ 1.0 (pH 2.5) to ≈ 0 (pH 8). Total quinoline concentration = 0.1 mM.

the neutral form. Zachara et al. (1986) also observed diminished adsorption of quinoline to low f_{oc} subsoils with increasing pH at pH > pK_a . Competition with protons (and/or readsorbed Al) for surface sites is the probable cause of diminished sorption as pH is decreased below the pK_a .

However, although increasing the organic matter content of the clays results in a more strongly acidic surface overall (i.e., decreased proton charge density at a given pH) it does not increase surface affinity for the quinolinium ion. Even at high pH, the presence of HA (and associated aromatic moieties) at the particle surface does not increase sorption of neutral quinoline. To the contrary, the “humic-free” kaolinite surface exhibits the highest affinity for this compound under all conditions (Fig. 3).

A large fraction of sorbed quinoline (the “nonextractable” fraction) was not desorbed during three successive 30-min extractions in 0.1 mol kg⁻¹ NH₄NO₃ solution (Fig. 4). The nonextractable fraction predominated at pH > pK_a . These data indicate that NH₄⁺ exchange of quinolinium is <100% effective at low pH, and the neutral compound is not readily desorbed into a dilute solution. Helmy et al. (1983) observed significant hysteresis in quinoline adsorption–desorption isotherms on Na-montmorillonite at pH 6, whereas Zhu et al. (1995) reported reversible sorption on a spent shale at pH

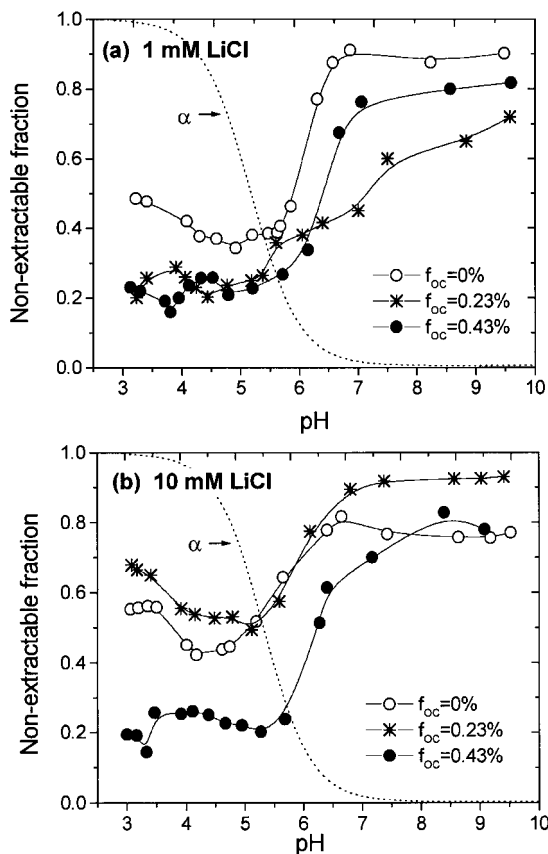


Fig. 4. The fraction of sorbed quinoline that was retained in the solid phase after three sequential extractions in unbuffered 0.1 M NH_4NO_3 solution following equilibration in (a) 1 mM LiCl and (b) 10 mM LiCl at the pH values shown. The dotted line represents the ionized fraction in solution ($[\text{QH}^+]/[\text{Q}]_T$) which decreases from ≈ 1.0 (pH 2.5) to ≈ 0 (pH 8).

8. In our experiment, regardless of the ionic strength conditions of adsorption, the nonextractable fraction was consistently higher for $f_{oc} = 0\%$ than for $f_{oc} = 0.43\%$, suggesting that quinoline sorbs to mineral-bound humic substances less strongly than to the kaolinite surface itself.

Lithium \rightarrow Quinoline Exchange

In the acid pH range, adsorption of QH^+ predominates and a conditional selectivity coefficient, K_{exc} , for $\text{Li}^+ \rightarrow \text{QH}^+$ exchange may be calculated for the exchange reaction:



where X represents one mole of cation exchanger charge. The value of K_{exc} is determined from:

$$K_{exc} = ([\text{QHX}]\gamma_{\text{Li}^+}m_{\text{Li}^+})/[\text{LiX}]\gamma_{\text{QH}^+}m_{\text{QH}^+} \quad [6]$$

where the surface concentrations are assumed equal to the surface excess of Li^+ (q_{Li} , Eq. [2]) and QH^+ ($\Gamma_{\text{QH}^+} = \alpha\Gamma_0$), and solution phase activity coefficients are calculated with the Davies equation. The K_{exc} values calculated for each pH are conditional because the rational activity coefficients of the adsorbed species are unknown (Sposito, 1994). In addition, the concentration

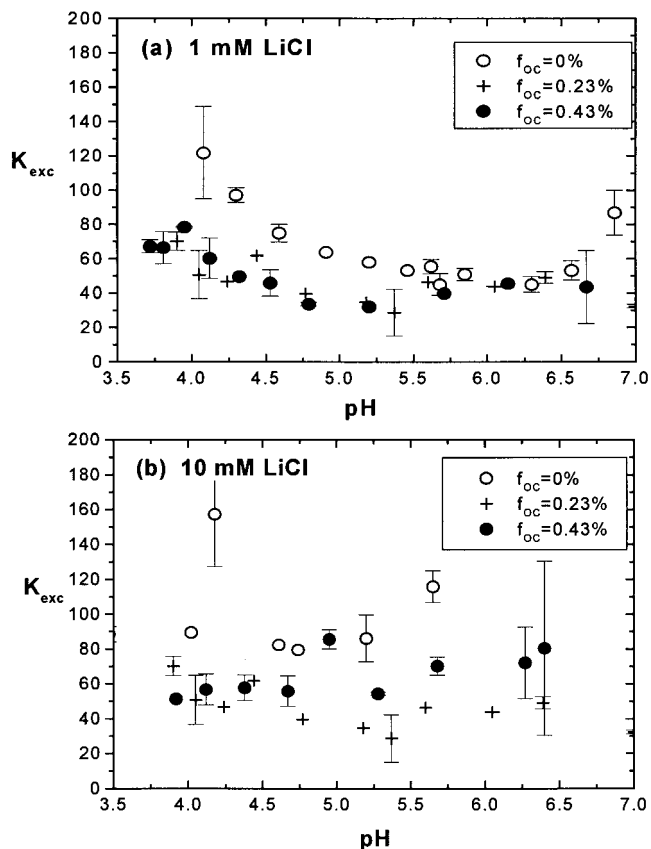


Fig. 5. Conditional selectivity coefficients for $\text{Li}^+ \rightarrow \text{QH}^+$ exchange as a function of pH and f_{oc} at 25°: (a) 1 mM LiCl, (b) 10 mM LiCl.

of available cation-exchange sites (X) increases with pH because of proton desorption (Fig. 2).

Calculated values of K_{exc} exhibit a clear pH dependence at low ionic strength; selectivity for QH^+ is highest for uncoated kaolinite and decreases from 120 to 45 with increasing pH from 3.5 to 6 (Fig. 5a). Values for K_{exc} on kaolinite-humic complexes in 1.0 mM LiCl range from ≈ 70 (pH 3.5) to 35 (pH 5.3). Data are more scattered at higher ionic strength and exhibit less pH dependence (Fig. 5b), but K_{exc} is consistently in the range of 80 to 120 for uncoated kaolinite and 40 to 80 for kaolinite-humic complexes. Ainsworth et al. (1987) found conditional K_{exc} for $\text{Na}^+ \rightarrow \text{QH}^+$ exchange on montmorillonite varied from 350 to 1200 as the mole fraction of adsorbed QH^+ ($[\text{QH}X]/[\text{QH}X + \text{Na}X]$) was decreased from 0.5 to 0.02 at pH 5 in 10 mM NaClO_4 solution. In our study, the mole fraction of adsorbed quinoline ($[\text{QH}X]/[\text{QH}X + \text{Li}X]$) decreased from ≈ 1.0 to 0.01 in all cases as a direct function of increasing pH from 3.5 to 7.0, but relatively smaller variation in K_{exc} was observed (Fig. 5). Since exchange preference for Li^+ vs. Na^+ on layer silicates is negligible (McBride, 1994), comparison of the K_{exc} values presented here with those reported by Ainsworth et al. (1987) shows that montmorillonite exhibits a higher selectivity for QH^+ than does kaolinite, and K_{exc} for kaolinite is further reduced by adsorption of humic substances. These results indicate an important role of charged siloxane sites in the preferential adsorption of this NHC.

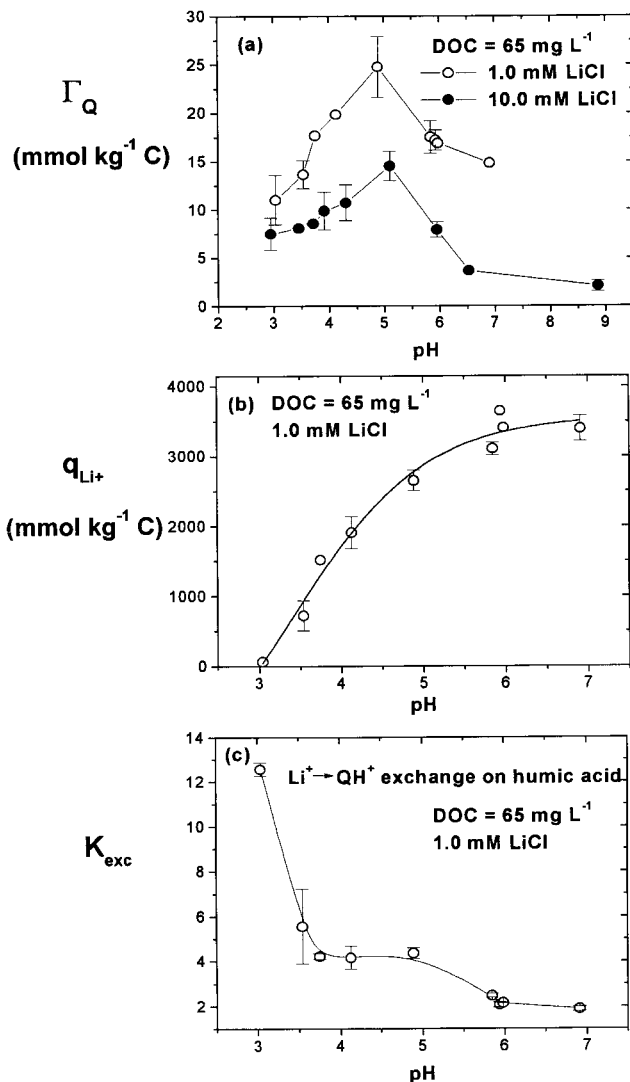


Fig. 6. Sorption of quinoline and Li^+ on humic acid at 25°C. (a) Sorption of quinoline to humic acid as a function of pH and ionic strength (total system quinoline concentration = $2.4 \mu\text{mol kg}^{-1}$). (b) Adsorption edge for Li^+ on humic acid (1.0 mM ionic strength). (c) Conditional selectivity coefficients for $\text{Li}^+ \rightarrow \text{QH}^+$ exchange on humic acid as a function of pH.

Quinoline Sorption to Humic Acid

Independent sorption dialysis experiments were conducted to study quinoline–humic interactions in the absence of kaolinite to verify the negative effect of HA on sorption to kaolinite (Fig. 6). The pH and ionic strength dependence of sorption to HA is similar to that reported for kaolinite and kaolinite–humic complexes (Fig. 3), with Γ_{max} occurring in the region of the pK_a for quinoline. Quinoline sorption is decreased by as much as 55% with increasing ionic strength from 1 to 10 mM, because of increased Li^+ competition for sorption sites (Fig. 6a). Sorption of Li^+ to HA was measureable only for the low ionic strength systems because at 10 mM LiCl, small differences between large Li^+ concentrations both inside and outside of the dialysis membrane yielded inaccurate results. However, sorption of Li^+ to HA at low ionic strength shows a clear increasing trend with pH

(Fig. 6b). Values of q_{Li^+} increase with increasing HA functional group dissociation such that maximum sorption ($\text{mmol kg}^{-1} \text{C}$) approaches 70% of the carboxylic acidity (Table 1).

In the dialysis systems, quinoline is present in total concentrations several hundred-fold lower than Li^+ , and it is selectively adsorbed to HA; K_{exc} values are >1 (Fig. 6c). However, selectivity for $\text{Li}^+ \rightarrow \text{QH}^+$ exchange on HA at any pH is significantly lower than on kaolinite and kaolinite–humic complexes (Fig. 5), an observation that supports the negative effect of sorbed HA on quinoline retention at the kaolinite surface. Prior research has shown that paraquat and diquat (aromatic N-containing cations) are also adsorbed selectively over monovalent and divalent cations on soil clays (Weed and Weber, 1969; Dixon et al., 1970). Although similar results have been reported for cation exchange of paraquat on soil organic matter (Burns et al., 1973), lower selectivity is observed.

Bellin and Rao (1993) reported that the sorption of quinoline to subsurface smectitic soils at pH 6 to 7 was reduced, whereas the sorption of Ca^{2+} (from background electrolyte) was unchanged, following inoculation of sterile smectitic soils (native $f_{\text{OC}} = 0.16\%$) with negatively charged bacterial cells. Since the cation (Ca^{2+})-exchange capacity was apparently unaffected by bacterial sorption, decreased quinoline retention was attributed to a hypothetical increase in solid–water interfacial pH upon sorption of cells to mineral surfaces. Re-evaluation of their results in light of our study suggests that lower quinoline affinity for the biofilms relative to the sterile mineral surfaces may result from inherent differences in the affinity of quinoline for mineral vs. organic functional groups.

CONCLUSIONS

Competition with Li^+ on cation exchange sites accounts for differential sorption of the quinolinium cation to kaolinite, HA, and kaolinite–humic complexes. Sorption of the cationic species is greater than for the neutral compound on both kaolinite and HA. Despite the increase in cation exchange that results when the kaolinite surface is modified by the adsorption of HA, quinoline is more competitive for sorption, and sorption is less reversible, on negatively charged sites of the kaolinite surface than on dissociated functional groups of HA. These data suggest that the neutral form of quinoline is relatively mobile in subsurface environments and that sorption of the cationic form will probably be lower in soils with high organic matter contents.

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REFERENCES

- Ainsworth, C.C., J.M. Zachara, and R.L. Schmidt. 1987. Quinoline sorption on Na-montmorillonite: Contributions of the protonated and neutral species. *Clays Clay Miner.* 35:121–128.

- Anderson, S.J., and G. Sposito. 1991. Cesium adsorption method for measuring accessible structural surface charge. *Soil Sci. Soc. Am. J.* 55:1569-1576.
- Barak, P., and Y. Chen. 1992. Equivalent radii of humic macromolecules from acid-base titration. *Soil Sci.* 154:184-195.
- Bellin, C.A., and P.S.C. Rao. 1993. Impact of microbial biomass on contaminant sorption and transport in a subsurface soil. *Appl. Environ. Microbiol.* 59:1813-1820.
- Bowles, E.C., R.C. Antweiler, and P. MacCarthy. 1989. Acid-base titration and hydrolysis of Suwanee River fulvic acid. p. 205-230. *In* R.C. Averett et al. (ed.) *Humic substances in the Suwannee River, Georgia; Interactions, properties and proposed structures*. U.S. Geol. Surv. Open File Rep. no. 87-557. U.S. Geol. Surv., Denver, CO.
- Burns, I.G., M.H.G. Hayes, and M. Stacey. 1973. Some physicochemical interactions of paraquat with soil organic materials and model compounds. *Weed Res.* 13:79-90.
- Carroll-Webb, S.A., and J.V. Walther. 1988. A surface complex reaction model for the pH-dependence of corundum and kaolinite dissolution rates. *Geochim. Cosmochim. Acta* 52:2609-2623.
- Chiou, C.T. 1989. Theoretical considerations of the partition uptake of nonionic organic compounds by soil organic matter. p. 1-29. *In* B.L. Sawhney and K. Brown (ed.) *Reactions and movement of organic chemicals in soil*. SSSA Spec. Publ. 22. SSSA and ASA, Madison, WI.
- Chorover, J., and G. Sposito. 1995. Surface charge characteristics of kaolinitic tropical soils. *Geochim. Cosmochim. Acta* 59:875-884.
- Davis, J.A. 1982. Adsorption of natural dissolved organic matter at the oxide/water interface. *Geochim. Cosmochim. Acta* 46:2381-2393.
- Dixon, J.B., D.E. Moore, N.P. Agnihotri, and D. Lewis. 1970. Exchange of diquat in soil clays, vermiculite and smectite. *Soil Sci. Soc. Am. Proc.* 34:805-808.
- Hassett, J.J., W.L. Banwart, S.G. Wood, and J.C. Means. 1981. Sorption of α -naphthol: Implications concerning the limits of hydrophobic sorption. *Soil Sci. Soc. Am. J.* 45:38-42.
- Helmy, A.K., S.G. De Bussetti, and E.A. Ferreiro. 1983. Adsorption of quinoline from aqueous solutions by some clays and oxides. *Clays Clay Miner.* 31:29-36.
- Karickhoff, S.W. 1984. Organic pollutant sorption in aquatic systems. *J. Hydraul. Eng.* 110:707-735.
- Kraepiel, A.M., K. Keller, and F.M.M. Morel. 1998. On the acid-base chemistry of permanently charged minerals. *Environ. Sci. Technol.* 32:2829-2838.
- Kretzschmar, R., D. Hesterberg, and H. Sticher. 1997. Effects of adsorbed humic acid on surface charge and flocculation of kaolinite. *Soil Sci. Soc. Am. J.* 61:101-108.
- McBride, M.B. 1994. *Environmental chemistry of soils*. Oxford Univ. Press, New York.
- Means, J.C., S.G. Wood, J.J. Hassett, and W.L. Banwart. 1980. Sorption of polynuclear aromatic hydrocarbons by sediments and soils. *Environ. Sci. Technol.* 14:1524-1528.
- Murphy, E.M., J.M. Zachara, S.C. Smith, J.L. Phillips, and T.W. Wietzma. 1994. Interaction of hydrophobic organic compounds with mineral-bound humic substances. *Environ. Sci. Technol.* 28:1291-1299.
- Nielsen, T., K. Siigur, C. Helweg, O. Jørgensen, P.E. Hansen, and U. Kirso. 1997. Sorption of polycyclic aromatic compounds to humic acid as studied by high-performance liquid chromatography. *Environ. Sci. Technol.* 31:1102-1108.
- Schlautman, M.A., and J.J. Morgan. 1993. Binding of a fluorescent hydrophobic organic probe by dissolved humic substances and organically-coated aluminum oxide surfaces. *Environ. Sci. Technol.* 27:2523-2532.
- Schwarzenbach, R.P., P.M. Gschwend, and D.M. Imboden. 1993. *Environmental organic chemistry*. John Wiley and Sons, New York.
- Schwarzenbach, R.P., and J. Westall. 1981. Transport of nonpolar organic compounds from surface water to groundwater: Laboratory sorption studies. *Environ. Sci. Technol.* 15:1360-1367.
- Southworth, G.R., and J.L. Keller. 1984. Mobilization of azaarenes from wastewater treatment plant biosludge. *Bull. Environ. Contam. Toxicol.* 32:445-452.
- Sposito, G. 1992. Characterization of particle surface charge. p. 291-314. *In* J. Buffle and H.P. van Leuwen (ed.) *Environmental particles*. Vol. 1. Lewis Publ., Boca Raton, FL.
- Sposito, G. 1994. *Chemical equilibria and kinetics in soils*. Oxford Univ. Press, New York.
- Stevenson, F.J. 1994. *Humus chemistry*. 2nd ed. John Wiley & Sons, New York.
- Stumm, W., and J.J. Morgan. 1996. *Aquatic chemistry*. 3rd ed. John Wiley & Sons, New York.
- Swift, R.S. 1996. Organic matter characterization. p. 1011-1069. *In* D.L. Sparks (ed.) *Methods of soil analysis*. Part 3. SSSA Book Ser. 5 SSSA and ASA, Madison, WI.
- Weed, S.B., and J.B. Weber. 1969. The effect of cation exchange capacity on the retention of diquat and paraquat by three-layer type clay minerals. I. Adsorption and release. *Soil Sci. Soc. Am. Proc.* 33:379-385.
- Wershaw, R.L. 1991. The importance of humic substance-mineral particle complexes in the modeling of contaminant transport in sediment-water systems. p. 23-34. *In* R.A. Baker (ed.) *Organic substances and sediments in water*. 1. Humics and Soils. Lewis, Chelsea, MI.
- Wieland, E., and W. Stumm. 1992. Dissolution kinetics of kaolinite in acidic aqueous solutions at 25°C. *Geochim. Cosmochim. Acta* 56:3339-3355.
- Zachara, J.M., C.C. Ainsworth, C.E. Cowan, and B.L. Thomas. 1987. Sorption of binary mixtures of aromatic nitrogen heterocyclic compounds on subsurface materials. *Environ. Sci. Technol.* 21:397-402.
- Zachara, J.M., C.C. Ainsworth, L.J. Felice, and C.T. Resch. 1986. Quinoline sorption to subsurface materials: Role of pH and retention of the organic cation. *Environ. Sci. Technol.* 20:620-627.
- Zhang, Z.Z., P.F. Low, J.H. Cushman, and C.B. Roth. 1990. Adsorption and heat of adsorption of organic compounds on montmorillonite from aqueous solution. *Soil Sci. Soc. Am. J.* 54:59-66.
- Zhu, S., P.R.F. Bell, and P.F. Greenfield. 1995. Quinoline adsorption onto combusted rundle spent shale in dilute aqueous solution at the natural pH 8. *Water Res.* 29:1393-1400.