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Quinoline Sorption to Subsurface Materials: Role of pH and Retention of the Organic Cation

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■ The sorption of quinoline (pK_a = 4.94) was investigated on low-organic-carbon subsurface materials that varied in pH. Sorption isotherms were measured from 10^{-7} to 10^{-4} M quinoline and were found to be nonlinear. The resulting Freundlich constants (K_F), based on total aqueous quinoline concentration, were poorly correlated with subsoil properties, including organic carbon. Higher sorption in the acidic subsoils and favorable coefficents for regression of K_F, normalized to cation-exchange capacity vs. the ionization fraction (Q), point to the importance of ion exchange of the protonated compound. When the subsoil pH is adjusted, it is shown that sorption parallels the ionization fraction and retention of the organic cation far exceeds that of the neutral species. Calculations of surface speciation and thermodynamic parameters of sorption ($\Delta H°$, $\Delta S°$) point to ion exchange and/or surface protonation at pH levels exceeding pK_a by greater than 2 log units. It is suggested that in subsurface materials of low carbon content, quinoline sorption is controlled by pH, the nature and capacity of the exchange complex, and groundwater ion composition.

Introduction

Basic nitrogen-heterocyclic compounds (NHC's) are common to many products and waste materials from energy development technologies. Within this general compound class, quinoline is especially important from an environmental health perspective, because it exhibits both high solubility in water and the potential to induce liver carcinoma. Quinoline and numerous alkylated isomers have been identified in energy-derived waste materials slated for in-ground disposal, particularly solid and liquid wastes from coal gasification (*1–4*) and shale oil extraction (*5*). The water solubility of the compound suggests that, in the event of intruding groundwater, quinoline may be leached from the wastes and enter the subsurface environment. In fact, quinoline has been observed in groundwaters proximate to underground coal gasification sites (*6, 7*). To a large degree, the subsurface dissemination of quinoline is controlled by sorption processes that may reduce the rate of compound movement relative to the transporting water front.

The soil or subsurface adsorption of multiring basic NHC's has not been investigated in great detail, and information on quinoline sorption by natural heterogeneous adsorbents is absent. As observed for many organic compounds, limited research with higher molecular weight quinoline analogues attests to the importance of organic carbon in sorption. In soils and sediments at pH values above pK_a, acridine and biquinoline sorption follow the K_{oc}–K_{ow} and K_{oc}–S relationships (*8, 9*) commonly observed for "neutral" aromatic compounds (*10, 11*). In contrast, an investigation of the soil sorption of benzidine, an aromatic amine, has demonstrated the important influence of organic compound protonation and the presence of the organic cation in the overall sorption process (*12*). Similarly, studies with layer silicates and oxides demonstrate the high sensitivity of quinoline adsorption to pH and

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suggest the dominant role of cationic sorption near and below the pK_a (pH 4.94) (*13*, *14*).

In view of the importance of NHC's in energy wastes and the lack of information on quinoline behavior in subsoil and groundwater, the present study was undertaken to investigate the magnitude and nature of quinoline sorption on subsurface materials. Batch adsorption and desorption studies using subsoils low in organic carbon and spanning a range in pH (4–8.5) were used to show the dominant role of the protonated quinoline form in compound adsorption even when solution pH exceeds the pK_a. The temperature dependency of adsorption over ranges including those of normal groundwaters and subsurface environments (5–35 °C) was used to calculate thermodynamic properties of quinoline adsorption and substantiate the proposed sorption mechanism. The results point to the importance of the ionization fraction and low sorption of the neutral compound, therefore suggesting that quinoline mobility will be high in subsurface environments with pH above neutrality.

Experimental Procedures

Subsoil Properties. Nine subsurface materials, with varied physicochemical properties, were selected for study. The group included lower B and C soil horizons, unconsolidated vadose zone materials, and aquifer materials herein termed subsoils for expediency. The subsoils were obtained primarily from regions where energy utilization or conversion facilities are currently located or will likely be situated in the future, including the Ohio Basin and central Appalachian coal regions (Loring, Elk, Westmoreland, Ft. Martin, and Dormont), the oil shale region of northwestern Colorado (Anvil Points), and the northern Great Plains lignite region (Zahl, Vebar). A wind-sorted sand from the banks of the Columbia River (Vernita) in Washington State was chosen as a model weak adsorbent.

Subsoil analyses and sorption studies were performed with air-dried, sieved materials (<2.0 mm). Total carbon was determined by induction furnace. Samples of each subsoil were then digested in HCl to remove carbonates, and organic carbon was measured by dry oxidation of the residue. A boiling KOH extraction (1 M, 30 min) was used to remove reactive organic carbon that was then quantified by UV-enhanced persulfate oxidation. Particle size distribution was determine d by sedimentation following sonic dispersion, with noncalcareous subsoils receiving a prior dithionite–citrate–bicarbonate treatment (*15*). External surface area was measured by multipoint N_2 adsorption and total surface area by ethylene glycol monomethyl ether (EGME) adsorption (*16*). The cation-exchange capacity (CEC) was determined by $^{45}Ca^{2+}$ exchange (*17*, *18*) on noncalcareous subsoils and by Li exchange (*19*) on calcareous subsoils.

Sorption Studies. (1) Compound Purity. Quinoline (99% purity, Aldrich Chemical Co.) was used without further purification. [^{14}C]Quinoline was custom synthesized (Pathfinders Laboratories) and further purified by liquid chromatography (Waters Associates, C-18 column, 25 cm × 3.9 mm) and a 40% acetonitrile/60% citrate buffer (0.05 M, 1:1 trisodium citrate–citric acid). The peak corresponding to quinoline was collected, partitioned into hexane, and back-extracted in 0.05 N HCl. The radiochemical purity was greater than 99%, and its specific activity was 9.72 mCi/mmol.

(2) Sorption–Desorption. Sorption studies were carried out in a batch mode at 25 °C in 25-mL Corex, high-speed centrifuge tubes with 2 g of soil and 10 mL of solution. Corex is a registered trademark of Corning Glass Works, Houghton Park, NY. A nitrogen atmosphere and N_2(g) sparged solutions were used to minimize the potential for aerobic microbiological degradation during the course of the experiments (*20*). The soil was preequilibrated with 0.01 M $CaCl_2$ for 4 h before the addition of quinoline. Varying quantities of cold quinoline standards were added to the soil solutions along with a fixed quantity of [^{14}C]quinoline (approximately 50 000 dpm). The initial concentration of quinoline ranged from 2.60×10^{-7} to 1.0×10^{-4} M. Each concentration was run in duplicate. After the quinoline was added, the centrifuge tubes were agitated in an incubator/shaker for 24 h. At the end of the incubation period, the tubes were centrifuged at 7500*g* for 15 min, and the supernatant was analyzed for radioactivity by liquid scintillation counting. The quantity of quinoline sorbed was determined by the difference between initial and final solution radioactivity measurements. Direct analysis of quinoline was performed selectively to corroborate counting data.

The selection of the 24-h equilibration period was based on a 72-h time course study (1:5 solid to solution ratio) with one quinoline concentration and two subsoils of differing pH. Direct quantification of quinoline by liquid chromatography over the 72-h period demonstrated that sorption equilibrium was attained rapidly in approximately 4 h and that abiotic/biologic transformation was minimal. The 24-h equilibration period for sorption was selected both for convenience and to assure that steady-state conditions were achieved for all subsoils.

Desorption measurements were made by conducting the sorption experiments as described above. After the 24-h incubation period under N_2 atmosphere, the supernatant (4 mL) was replaced with fresh 0.01 M $CaCl_2$ containing no quinoline and then agitated for an additional 4 h under N_2 at 25 °C. Again, 4 mL of supernatant was removed, counted, and replaced with fresh $CaCl_2$ solution and the process repeated over four cycles. Radioactivity measurements at the end of each 4-h equilibration were used to generate the desorption curve. A 48-h time course study, where a desorption cycle was initiated by replacing the equilibrium solutions of two subsoils that were loaded with one initial concentration of quinoline, demonstrated that little change in aqueous concentration occurred after a 4-h desorption period. It was recognized that although an apparent steady state was reached in 4 h, considerably longer time periods may have been required to attain equilibrium for the more strongly sorbing subsoils.

(3) pH-Dependent Sorption. To fully investigate the influence of pH, an acid and basic subsoil exhibiting the highest and lowest quinoline adsorption, respectively, were selected for further study. The basic soil was weakly calcareous but contained no detrital carbonate in the sand fraction. Sixteen samples (2 g) of each subsoil in the presence of 0.01 M $CaCl_2$ were adjusted to different pH levels by addition of 0.1 N CaOH or HCl and allowed to equilibrate under N_2 atmosphere. Following 24-h equilibration (25 °C), the supernatant was removed, the pH adjusted, and equilibration repeated. After a second 24-h equilibration, the supernatant was replaced with fresh 0.01 M $CaCl_2$, the pH was readjusted, and sorption studies were performed at 25 °C using 9.76×10^{-6} M quinoline. Final pH was measured after the sorption experiment.

(4) Influence of Temperature. Sorption isotherms were measured for two acid and two basic subsoils at additional temperatures (5, 15, 35 °C) to define the temperature-induced variation in sorption that may occur in typical subsurface systems (5–20 °C) and to develop thermodynamic parameters ($\Delta G°$, $\Delta H°$, $\Delta S°$) describing the sorption process. The sorption methodology described

Table I. Freundlich Constants for Quinoline Sorption on Subsurface Materials in the Presence of 0.01 M $CaCl_2$

subsoil	K, μmol^{1-N} g^{-1} mL^{Na}	N	r^2	K_{F2}, $\mu mol^{0.3}$ g^{-1} $mL^{0.7}$	N = 0.7, r^2
Elk	5.83	0.766	0.995	7.35	0.994
Dormont	3.18	0.656	0.999	3.56	0.998
Westmoreland	2.76	0.554	0.996	4.23	0.986
Loring	5.80	0.585	0.994	8.29	0.990
Ft. Martin	6.12	0.715	0.990	5.71	0.991
Vernita	0.411	0.614	0.993	0.518	0.975
Vebar	0.512	0.836	0.997	0.337	0.999
Anvil Points	1.13	0.907	0.999	0.655	0.993
Zahl	1.02	0.797	1.00	0.792	0.996

[a] See ref 46 for discussion of units associated with Freundlich constants.

previously was used with only slight modification to minimize headspace and compound volatilization at higher temperatures (35 °C). The batch equilibrations and subsequent centrifugation for phase separation were performed under carefully controlled temperature conditions (T = ±1 °C in a constant-temperature incubator–shaker and centrifuge).

Results and Discussion

Sorption. The quinoline adsorption isotherms were curvilinear on each of the nine subsoils. These (Figure 1) could be described by the Freundlich equation and gave good fits to the linear form of the equation:

$$\log S = \log K + N \log C_e \quad (1)$$

where K and N are constants specific to each subsoil, S = micromoles of quinoline adsorbed per gram of soil, and C_e = micromoles of quinoline per milliliter of solution. The quinoline Freundlich constants and linear correlation coefficients are given in Table I.

Banwart et al. (*8*) measured the sorption of two analogues of quinoline, namely, biquinoline and acridine, and found the sorption of these compounds in soils and sediment to correlate well with the percentage of soil organic carbon. Interestingly, quinoline showed no correlation (r^2 = 0.0100) with the organic carbon content of subsoils used in these studies. Moreover, the correlation was not improved by considering alkali-extractable organic carbon as is commonly observed for metal adsorption. An explanation for this behavior may be the relative hydrophobicity of the molecules. Quinoline has a water solubility

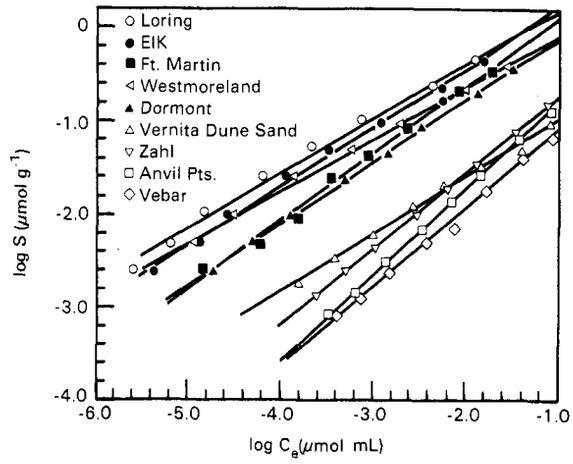

Figure 1. Quinoline sorption on subsurface materials (0.01 M $CaCl_2$) over the initial concentration range of 2.6 × 10^{-7}–1.0 × 10^{-4} M.

of 6000 mg kg^{-1} and an octanol/H_2O partition coefficient of approximately 107 (*21*). The water solubility of biquinoline and acridine are 1.02 and 38.4 mg kg^{-1}, respectively, and their octanol/H_2O partition coefficients are 20 200 and 4200, respectively. For the acridine and biquinoline, solvophobic forces in the aqueous phase may drive the sorption process, while for the more polar quinoline, site-specific electrostatic interactions with reactive surface functionalities on organic material and mineral surfaces become important. Another consideration is that, of the 14 soils used by Banwart et al. (*8*), only two had a pH below 6. In most of the soils studied, therefore, acridine and biquinoline exist in the neutral form allowing hydrophobic forces to predominate in compound sorption.

The low organic carbon content of the subsoils in this study may also play an important role. Some investigators have found good correlation between adsorption of hydrophobic and halogenated compounds and organic carbon content in low-organic-carbon soils and subsoils (*8*, *22–25*); others observe that the properties of the mineral fraction or pH become increasingly important when the compound is polar or ionizable (*12*, *26*).

An examination of the Freundlich constants (Table I) and the physical properties of each soil (Table II) reveals that pH exerts a major influence on the sorption of quinoline, with the acidic soils exhibiting the greatest sorption. In the acidic soils, quinoline (pK_a = 4.94) is predominantly

Table II. Selected Subsoil Properties

subsoil	organic C, % total	organic C, % extractable	particle distribution, % sand	silt	clay	surface area, m^2/g by N_2 adsorption	surface area, m^2/g by EGME	CEC (mequiv/100 g)	pH (H_2O)	pH (0.01 M $CaCl_2$)
Elk (Ultic Hapludalf, C horizon)[a]	0.22	0.16	11	57	32	27.2 ± 5.0	69.4 ± 3.2	6.7	4.23	3.72
Dormont (Ultic Hapludalf, C horizon/residuum)	0.26	0.19	9	54	37	34.2 ± 1.3	90.4 ± 2.8	7.37	4.63	4.26
Westmoreland (Ultic Hapludalf, B2t horizon)	0.20	0.13	37	43	20	20.2 ± 1.2	53.5 ± 1.2	3.8	4.75	4.18
Loring (Typic Fragiudalf, Bx2 horizon)	0.24	0.19	2	70	28	30.5 ± 1.0	66.9 ± 2.2	8.4	4.85	4.18
Ft. Martin (unconsolidated aquifer material)	0.74	0.17	14	54	32	27.4 ± 0.7	75.7 ± 0.8	10.9	5.19	5.27
Vernita (wind-sorted sand)	0.02	0.04	66	33	1	2.64 ± 0.03	16.4 ± 2.2	1.7	7.16	6.88
Vebar (Typic Haploboroll, C2 horizon and below)	0.35	0.15	75	11	14	9.20 ± 0.26	89.4 ± 1.2	11.23	8.00	7.46
Anvil Points (unconsolidated material overriding aquifer)	0.58	0.16	28	44	28	23.4 ± 0.4	65.4 ± 6.5	12.45	8.15	7.64
Zahl (Typic Argiboroll C2 horizon and below)	1.21	0.41	26	50	24	15.0 ± 0.3	86.6 ± 1.6	14.15	8.17	7.70

[a] Surface soil classification where appropriate, sample zone/horizon.

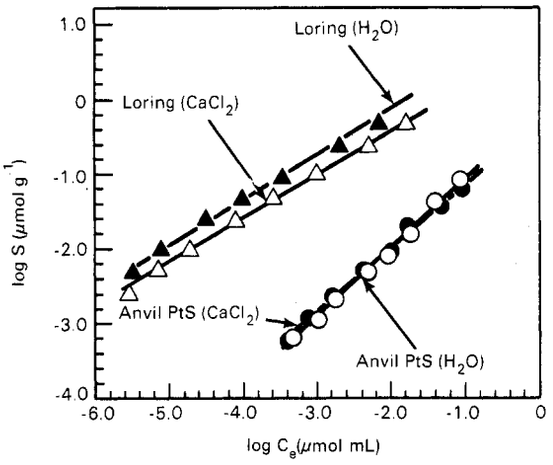

Figure 2. Quinoline sorption on acid and basic subsoils in distilled water and $CaCl_2$ (0.01 M).

in the protonated form. This suggests a cationic adsorption mechanism as the major mode of quinoline binding. However, the Freundlich constants did not correlate with solution hydrogen ion activity ($r^2 = 0.329$), even with K (K_{F2}) values from linearized Freundlich isotherms where N was forced to 0.7 (average N value for the nine soils used). The modified Freundlich constants (K_{F2}) did not demonstrate a significant correlation with clay content ($r^2 = 0.280$) or with total or external surface area ($r^2 = 0.571$).

The influence of the cationic species was further evaluated by regressing the ionization fraction, Q, of quinoline against K_{F2}

$$Q = \frac{[BH^+]}{[B + BH^+]} = \frac{1}{1 + K_a/[H^+]_w} \quad (2)$$

normalized to cation-exchange capacity (CEC in μmol g^{-1}), internal surface area (ISA; EGME–N_2 surface area in m^2 g^{-1}), and total surface area (TSA; EGME surface area in m^2 g^{-1}). The correlation coefficients point to the role of cation exchange; $r^2 = 0.977$ for Q vs. K_{F2}/CEC for subsoils with pH (0.01 M $CaCl_2$) below 7, and K_{F2} = CEC[0.0308 + 0.0826Q]. When all subsoils were used, a weaker correlation was observed for internal and total surface area; i.e., $r^2 = 0.831$ for Q vs. K_{F2}/TSA, and $r^2 = 0.847$ for Q vs. K_{F2}/ISA. The linear relationship between K_{CEC} and Q for soils below pH 7 suggest that, to a large degree, the Freundlich constants are a function of the CEC and the ionization fraction of the compound. Importantly, as Q decreases, K_{CEC} decreases concomitantly.

The correlation of quinoline adsorption with CEC, though universally observed for cations in soil, is surprising in this study where only low surface coverage was attained. Calculations suggest that at maximum quinoline sorption in all subsoils used, less than 1% of the cation-exchange equivalents are balanced by quinoline, assuming the presence of the protonated species. At such low surface coverage, surface charge density and other microscopic properties of the adsorbent surface should become equally or more important than total CEC. The influence of surface charge density and 2:1 mineral structure on adsorption of certain organic cations is well established (*27*, *28*).

The presence of a cationic adsorption mechanism is further substantiated by the decrease in quinoline adsorption that occurs in acid subsoils in the presence of increasing Ca^{2+} concentrations (data not shown). Increasing Ca^{2+} from 0.001 to 0.1 M significantly reduces quinoline adsorption (1.0×10^{-5} M initial concentration) by approximately 60% when the subsoil pH is near or below the compound pK_a. In acid subsoil, the Freundlich adsorption constant in 0.01 M $CaCl_2$ is half that observed in distilled, deionized H_2O (Figure 2). When the subsoil pH is significantly above the pK_a of quinoline (e.g., pH >7.0), the effects of 0.01 M $CaCl_2$ are negligible, as shown for the Anvil Points subsoil (Figure 2). These results suggest that Ca^{2+} competes with positively charged quinoline species for cation-exchange sites.

Desorption. The desorption of quinoline was examined on two acid and two basic subsoils, with two selected examples shown in Figure 3. In both subsoils, desorption shows significant hysteresis; however, it is pronounced in the more adsorbent, acidic subsoil. After four solution replacements, only 10.3% and 15.6% of the quinoline were desorbed at the lower and higher concentrations, respectively. In contrast, the Anvil Points subsoil exhibits significant reversibility, with 57.2% desorption occurring at low concentration and 60.3% at high concentration.

The normalization procedure of Rao et al. (*29*) was used to quantify the extent of hysteresis in the isotherms. A plot of relative adsorbed concentration (S/maximum adsorbed concentration) vs. relative solution concentration (C_e/maximum equilibrium solution concentration) eliminates the commonly observed dependency of the hysteresis index on the initial adsorbed concentration. Any point on the isotherm that exceeds the initial sorbed and equilibrium concentrations of all desorption loops may be selected to fix the maximum sorbed (S_m) and maximum solution

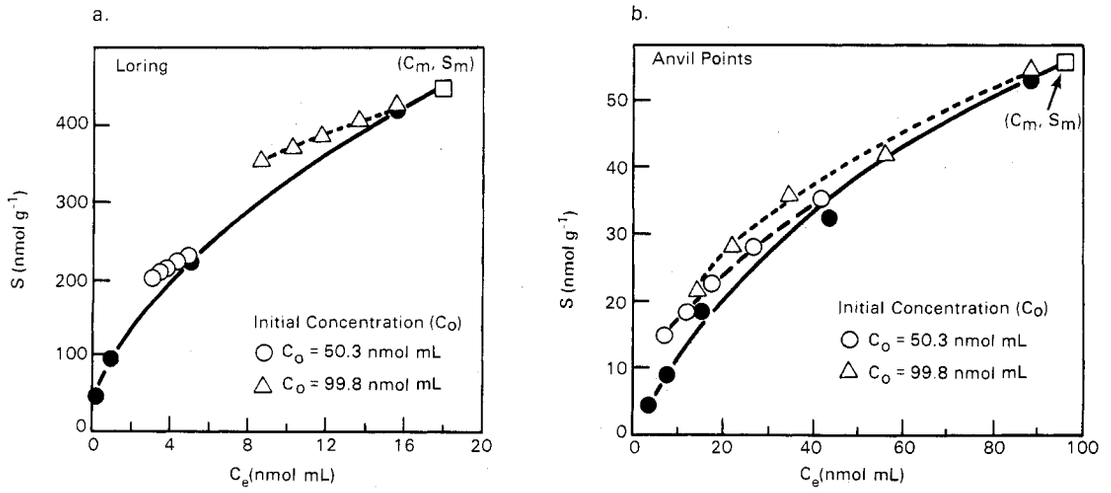

Figure 3. Quinoline desorption from acid and basic subsoils: (a) Loring subsoil; (b) Anvil Points subsoil.

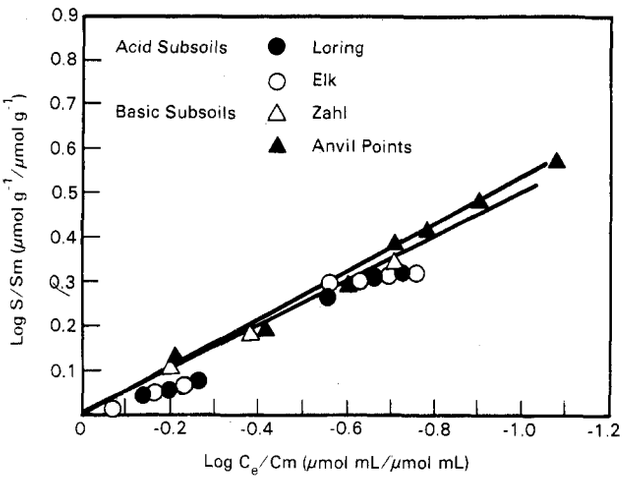

Figure 4. Normalized desorption isotherms of quinoline on acid and basic subsoils.

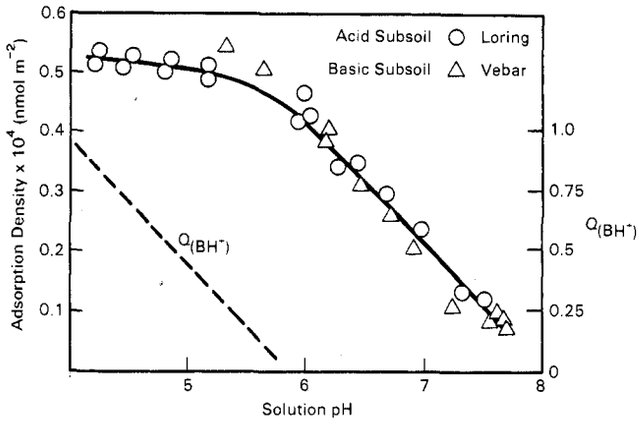

Figure 5. Influence of pH on adsorption density of quinoline (9.8×10^{-6} M) on acid and basic subsoils.

(C_m) concentrations for the normalization. The hysteresis index is defined as the ratio of Freundlich exponential parameters (N) for adsorption (N_a) and desorption (N_d) (hysteresis index = N_a/N_d). For Quinoline, the Rao et al. (*29*) procedure produces a linear relationship for the basic soils (Figure 4), yielding comparable indexes of desorption hysteresis (N_a/N_d = 1.71 for Zahl and 1.74 for Anvil Points subsoils). The two acid subsoils also behave consistently; however, desorption is clearly dependent on the initial adsorbed concentration, and an average index of hysteresis is not readily obtained.

Desorption hysteresis in sediment and soil has been ascribed to a number of physicochemical and biological factors, including microbiologic degradation (*20*, *30*), diffusion from internal regions or pore spaces of organic/mineral adsorbents (*31*, *32*), and changing properties (e.g., microparticulates, dissolved organic material) of the solid/liquid suspension with sequential equilibrium solution replacement (*33*, *34*). In this study, a N_2(g) atmosphere was used to minimize "apparent" hysteresis that may arise from aerobic microbiologic utilization of the desorbing compound as a carbon source. Poor reversibility was noted primarily in acidic subsoils where retention of the organic cation is presumed. This, and other evidence, suggests that abiotic factors control quinoline desorption hysteresis. In separate unpublished degradation experiments (*35*) at a lower solid-to-solution ratio (1:1) under N_2(g), quinoline was shown by direct analysis to be exceptionally stable in strongly sorbing acidic subsoils persisting in the unaltered form up to 12 months and for up to 3–4 months in weakly sorbing basic subsurface materials. This long-term behavior of quinoline is consistent with a high surface stability of the sorbed ionized compound and the poor reversibility noted in the desorption experiments. We may, therefore, ascribe desorption hysteresis to slow reequilibration rates for the surface–organic cation complex that is bound by both a localized electrostatic interaction and weak van der Waals forces between the multiple-ring structure and the solid surface. The hysteresis may be further accentuated by slow back-diffusion through sorbent interlayers or pore spaces of high tortuosity.

The desorption behavior of quinoline in subsoil compares favorably with that observed by using layer lattice silicates as adsorbents. Adsorption reversibility at intermediate pH values is low on layer silicates and decreases with decreasing pH, suggesting strong retention and limited desorbability of positively charged species (*13*, *14*). Similarly, poor adsorption reversibility is also noted for other aromatic organic cations on smectites where long-range, weak attractive forces stabilize the electrostatic interaction (*28*). The desorption of quinoline from basic subsoil exceeds that observed for smectites at a comparable pH. The hysteresis index for the basic subsoils ($N_a/N_d \sim 1.71$–1.74) is lower than observed for hydrophobically bonding pesticides in soil that conform to the $K_{oc} - K_{ow}$ relationship (*29*).

Role of pH. Quinoline is an organic base, which, when solution pH is below the compound pK_a, exists primarily as a cation. As shown in Figure 1, quinoline adsorption is markedly higher in acid subsoils, suggesting preferential adsorption of the cationic species. This hypothesis is further supported by the sorption behavior of quinoline as a function of pH in the Loring and Vebar subsoils. When adsorption is depicted as surface density on a total surface area basis (nmol m^{-2}), the pH-dependent adsorption behavior of the acid subsoil and that of basic subsoil become very similar (Figure 5), with adsorption decreasing sharply with increasing pH. These two subsoils supported the greatest and least amount of adsorption at their natural pH (Figure 1).

Although the pH-dependent sorption behavior of quinoline is likely a reflection of compound ionization, sorption does not decrease in direct response to the ionization fraction [$Q(BH^+)$, Figure 5]. In contrast, an inflection occurs at a pH approximately one full pH unit above the pK_a of the compound. Below this inflection point, sorption is relatively unaffected by a change in the ionization fraction of BH^+ from 0.9 to 0.25. Above this point, however, the decrease in quinoline sorption roughly parallels, but is less than, the decrease in ionization fraction. This pH-dependent behavior suggests enhanced protonation of quinoline at the sorption surface, a phenomenon noted for other organic bases (*36*–*38*). The depressed dielectric constant of vicinal water near clay mineral surfaces and enhanced Brønstead acidity of solvated exchangeable cations contribute to this proton transfer (*39*). Some even suggest that the "apparent surface acidity" of clay mineral surfaces may be 2–4 pH units below that of the bulk solution (*36*).

The Freundlich adsorption constants (K_{Fs}) for the ionized species were calculated at each pH to determine whether the measured adsorption could be described by using single values for the ionized and neutral species. The procedure of Zierath et al. (*12*) was used where the neutral species is assumed to adsorb only to the organic fraction in the subsoil. An average equilibrium partition coefficient (K_p) for each soil was estimated by using the K_{oc} regression equations of Banwart et al. (*8*) and Rao et al. (*29*), a quinoline solubility of 6000 mg kg^{-1}, K_{ow} of 107, and the

Table III. Variation in Freundlich Constants and Calculated Species Distribution for Loring Subsoil

pH	K_p, g^{-1} mL	K_{F2},[a] $\mu mol^{0.3}$ g^{-1} $mL^{0.7}$	K_{F3}, $\mu mol^{0.3}$ g^{-1} $mL^{0.7}$	HB_w^+/B_w	HB_s^+/B_s
4.25	0.105	10.68	12.3	4.46	46 375
4.47	0.105	9.73	12.1	2.70	26 285
4.86	0.105	8.75	13.7	1.09	13 035
5.17	0.105	6.54	13.6	0.536	6 418
6.04	0.105	2.73	17.9	0.0727	1 350
6.24	0.105	1.54	13.6	0.0456	643.4
6.63	0.105	1.15	18.6	0.0186	468.9
7.49	0.105	0.302	18.1	0.00256	90.66

[a] $S = K_{F2}C_e^{0.7}$.

organic carbon content of the subsoil. These K_p values were used along with ionization fraction (Q, eq 2) and the following equations to calculate Freundlich constants for the ionized species (K_{F3}, Table III) with N forced to 0.7.

$$B_w \rightleftarrows B_s \qquad K_p = \frac{[B_s]}{[B_w]} \tag{3}$$

$$HB_w^+ \rightleftarrows B_w + H^+ \qquad K_a = \frac{[B_w][H^+]\gamma^\circ\gamma^+}{[HB_w^+]\gamma^+} \tag{4}$$

$$0.7HB_w^+ \rightleftarrows HB_s^+ \qquad K_{F3} = \frac{[HB_s^+]}{[HB_w^+]^{0.7}} \tag{5}$$

$$[B_s^*] = [B_s] + [HB_s^+] \tag{6}$$

$$[B_w^*] = [B_w] + [HB_w^+] \tag{7}$$

$$[B_s^*] = K_F[B_w^*]^N \tag{8}$$

$$[B_s^*] = K_{F2}[B_w^*]^{0.7} \tag{9}$$

The subscripts w and s refer to water and subsoil, the brackets refer to concentration, B and HB^+ refer to the neutral and protonated species of quinoline, and the asterisks refer to total water-bound or subsoil-bound concentrations at equilibrium.

The calculated species distribution for the ionized molecules on the subsoil surface ($[HB_s^+]/[B_s]$, Table III) demonstrates the dominant influence of the cationic species in adsorption, even when the ionization fraction is low. These results suggest that the protonated species dominates the adsorption complex in excess of two pH units above the pK_a. This behavior arises from the much stronger affinity of the subsoil for the cationic species, and enhanced interfacial protonation. Similar behavior was found for the basic subsoil, but the regression equations for K_{oc} lead to an overestimate of K_p (0.154 estimated vs. 0.130 observed). It is important to note that K_{F3} is not constant over the pH range and reaches a maximum over pH 6.50. Clearly, many factors may influence the adsorption of the ionized species and K_{F3}, including competing cations (H^+, Al^{3+}, Ca^{2+}), inorganic ligands capable of ion pairing, and formation of quinoline hemisalts near the pK_a. These factors, combined with the experimental observations that K_{F3} is not single valued over a range in pH in a given subsoil suggest that predictive relationships [for example, those established by Pionke and DeAngelis (*40*)], which assume a single value of K_{F3}, may lead to erroneous results for soil or earth materials with low organic carbon.

A major source of uncertainty in the calculations of data in Table III is the assumption that sorption of the neutral quinoline species is governed by partitioning to the subsoil organic phase and that the log ($K_{ow} - K_{oc}$) relationship is an adequate predictor of this phenomenon. Limited evidence suggests that sorption to "hydrophobic" mineral surfaces may be of importance in low-carbon materials (*41*). The siloxane surface of layer lattice silicates with low-charge density (smectites) but high surface area may be particularly important in this respect (*22*). The trend of increasing Freundlich constants for the ionized species (K_{F3}, Table III) may therefore reflect a low predicted K_p value for the neutral compound. It is probable that sorption of the neutral quinoline molecule in these low-carbon subsoils is controlled not only by particulate organic material but also by hydrophobic mineral surfaces as well.

Temperature Dependency. Quinoline adsorption was measured from 5 to 35 °C on two acidic and basic subsoils to evaluate the thermodynamics of adsorption. The temperature range includes and exceeds the normal range observed in subsoil and groundwater (5–20 °C). The influence of temperature was comparable for all subsoils, with highest adsorption occurring at 5 °C and decreasing to 35 °C, thus suggesting the exothermic nature of the overall adsorption process. The thermodynamic equilibrium constant (K_0) and the standard free energy ($\Delta G°$ in kcal mol^{-1}), entropy ($\Delta S°$ in cal mol^{-1} deg^{-1}), and enthalpy ($\Delta H°$ in kcal mol^{-1}) of adsorption (Table IV) were calculated from the methods of Biggar and Cheung (*42*) and Moreale and van Bladel (*43*).

It is immediately apparent that the higher quinoline adsorption observed in the acidic subsoils is reflected in a large K_0, $\Delta G°$, and $\Delta H°$. For all subsoils, $\Delta H°$ is negative, suggesting the net adsorption process (e.g., combined influence of solute adsorption, solvent desorption, and molecular diffusion) is exothermic. The differences in $\Delta G°$, $\Delta H°$, and $\Delta S°$ between subsoils primarily reflect adsorption of quinoline as the protonated or cationic form in the acid materials and as the neutral molecular form in the basic subsoil. The large $\Delta G°$ and negative $\Delta H°$ and $\Delta S°$ for the Loring subsoil are symptomatic of an ion-exchange mechanism, while the lower $\Delta H°$ in the basic subsoil is comparable to the range cited for hydrogen bonding [−2 to −4 kcal mol^{-1} (*42*)]. In contrast to many hydrophobic

Table IV. Calculated Thermodynamic Parameters for Quinoline Adsorption

subsoil	temp, °C	$K_0 \times 10^3$ [a]	$\Delta G°$, kcal mol^{-1}	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, cal mol^{-1} K^{-1}
Loring	5	102.7	−6.374		
	15	73.86	−6.415		
				−7.096	−2.45 ± 0.109
	25	48.53	−6.389		
	35	31.26	−6.334		
Anvil Points	15	0.1025	−2.649		
	25	0.0865	−2.640	−2.89	−0.833 ± 0.009
	35	0.0744	−2.637		

[a] $K_0 = a_s/a_e = \gamma_s C_s/(\gamma_e C_e)$ where a = activity ($\mu g\ cm^{-3}$), γ = activity coefficient, C_e = concentration of the solute in equilibrium solution ($\mu g\ cm^{-3}$), and C_s = concentration of the adsorbed solute per unit of solvent in contact with the adsorbent surface ($\mu g\ cm^{-3}$).

compounds, $\Delta S°$ values for both soils indicate that quinoline exhibits greater orientation or less freedom in the sorbed state than when solvated. This effect is most distinct when sorption of the protonated form occurs.

The reported thermodynamic values for quinoline adsorption on low-carbon subsoils differ from values observed for compounds that are structurally similar on soils. In contrast to quinoline, aniline (pK_a = 4.93) adsorbs with positive $\Delta H°$ in surface soils with pH above and below the compound pK_a (*43*). This anomalous heat of adsorption was explained by the suggestion that the overall energetics of aniline retention in surface soils are controlled not by the sorption reaction, which is exothermic, but rather by diffusion to sorption sites in porous aggregates of organic material, which is encouraged as temperature increases. Naphthalene, a hydrophobic, two-ring, aromatic compound, differs from both quinoline and aniline in that it is adsorbed in soil via an entropy-driven reaction [$\Delta S°$ = +10–18 cal mol^{-1} K^{-1} (*44*)]. The negative $\Delta S°$ and $\Delta H°$ values for quinoline in the basic soils suggest that even when it is predominantly neutral, quinoline is not adsorbing as a "hydrophobic" solute. Rather, these calculations qualitatively substantiate the conclusion from Table III that the cationic species predominates—or at least strongly influences—the nature of the adsorption complex at solution pHs significantly above pK_a.

Conclusions

Batch equilibrium studies with subsurface materials indicate that quinoline sorption is controlled by ion exchange of the protonated cationic species over much of the natural groundwater pH range. Unlike higher molecular weight aromatic NHC's, weight fraction of organic carbon is not an accurate predictor of quinoline sorption.

The compound pK_a serves as a poor indicator of the solution pH range where exchange predominates. Calculations indicate that the protonated species dominates the surface complex, even when pH exceeds the pK_a by 2 pH units. This proposed surface speciation suggests enhanced protonation of quinoline near the sorption surface and emphasizes the more favorable energetics that drive sorption of the protonated species. The observed enthalpy component of sorption in the higher pH subsoils is at least partially consistent with retention by ionic or dipolar interaction.

Quinoline sorption in subsurface materials with pH below neutrality is influenced by solution and exchangeable inorganic cations that compete for negatively charged surface sites. Freundlich absorption constants vary with these properties and may be of limited use in describing sorption in subsurface systems. Selectivity coefficients (e.g., see ref 45) and thermodynamic exchange constants for the protonated species

$$BH^+ + {}^1/_2CaX_2 \rightleftarrows BHX + {}^1/_2Ca^{2+} \qquad (10)$$

probably represent the most accurate and versatile descriptors of the dominant mechanism of sorption.

In direct contrast to the observed strong retention of the organic cation, the neutral quinoline molecule is weakly sorbed when particulate organic carbon is low. This low sorption is a reflection of the dipole moment of quinoline, which facilitates solvation of the neutral compound by water, and a relatively low cavity energy in water. These jointly produce a weak solvophobic force driving sorption. As a result of this contrasting sorption behavior of the cationic and neutral form, quinoline will exhibit low mobility in groundwater of acid and weakly acid pH and high mobility in calcareous or basic subsurface systems with low particulate organic carbon. To fully understand the transport behavior of quinoline in the subsurface, additional work is needed on the exchange reaction, the influence of competing cations, and the importance of sorption of the neutral species by subsurface mineral surfaces.

Registry No. C, 7440-44-0; quinoline, 91-22-5; protonated quinoline, 22559-70-2.

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Interaction of Gold(I) and Gold(III) Complexes with Algal Biomass

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■ *Chlorella vulgaris* accumulates both gold(I) and gold(III) from aqueous solutions with high affinity. The degree of gold adsorption strongly depends on competing ligands present in the solution. Tetrachloroaurate(III) and gold(I) sodium thiomalate are rapidly adsorbed by the algal cells over a wide pH range, whereas dicyanoaurate(I) is bound more slowly and in a highly pH-dependent manner, with maximum binding observed near pH 3.0. Inhibition and reversal of gold binding by strong competing ligands (mercaptoethanol, cyanide, and thiourea) are also pH dependent. Under certain conditions, the level of gold accumulation by *Chlorella vulgaris* approaches 10% of the organism's dry weight. Experiments suggest that the alga rapidly reduces gold(III) to gold(I) and that the algal-bound gold is slowly reduced to gold(0).

Introduction

Metal ions including Pb(II), Cu(II), Ni(II), Zn(II), Cd(II), Ag(I), Hg(II), and U(VI) may be strongly adsorbed on the cell surfaces of algae (*1-6*), fungi (*7*), and bacteria (*8*). In fact, several studies suggest that biomass, which can be produced at low cost, might be a valuable aid in the treatment of contaminated waters and recovery of metal ions in mining operations. Relatively few reports, however, appear on the interaction of gold or other precious metal ions with microorganisms (*5, 6, 8-11*). Since the chemistry of gold(I) and gold(III) differs significantly from that of most other metal ions, the gold-sequestering process is expected to exhibit unique characteristics. A method for the recovery of gold ions from waters, which utilizes the adsorptive properties of a biomass, might be useful under certain conditions. Herein, we present a systematic study of experimental conditions that affect the interactions of tetrachloroaurate(III), dicyanoaurate(I), gold(I) sodium thiomalate, and other gold complexes with lyophilized *Chlorella vulgaris*.

An important mechanism for the accumulation of metal ions by algae and other microorganisms is biosorption, in which metal ions in solution are adsorbed on the surface of a microorganism through interactions with chemical functional groups found in the cell wall biopolymers. Biosorptive interactions may occur with either living or dead organisms, and do not necessarily require biological activity. Potential binding sites on the cell surfaces include amines, amides, imidazoles, hydroxyls, carboxylates, phosphates, thiols, thioethers, and other functional groups. The chemical composition of *Chlorella vulgaris* cell walls is complex, but major quantities of polysaccharides, uronic acids, and proteins (*12*) offer a range of potential binding sites for metal ions. It is, therefore, possible that the binding of metal ions to *Chlorella* may occur to a number of different kinds of sites.

Reviews on the chemistry of gold compounds in aqueous and biological systems appear elsewhere (*13-15*). However, it is relevant to describe some chemical characteristics of the gold complexes that we have tested in experiments with *Chlorella vulgaris*.

Gold(I) and gold(III) are classified as "class b" or "soft" metal ions, since the strength of coordination to halide

Table I. Formation Constants for Gold(I) and Gold(III) Complexes

species	log formation constant[a]	ref
$AuCl_2^-$	$k_1 = 12.15$, $k_2 = 7.79$, $\beta_2 = 19.94$	13
$AuBr_2^-$	$k_1 = 11.98$, $k_2 = 8.41$, $\beta_2 = 20.39$	13
AuI_2^-	$k_1 = 17.1$, $k_2 = 6.7$, $\beta_2 = 23.8$	13
$Au(CN)_2^-$	$\beta_2 = 33.7$	13
$Au(NH_3)_2^+$	$k_1 = 10.14$, $k_2 = 8.0$, $\beta_2 = 18.14$	13
$Au(SCN_2H_4)_2^+$	$\beta_2 = 21.3$	17
$AuCl_4^-$	$k_1 = 9.26$, $k_2 = 8.31$, $k_3 = 7.31$, $k_4 = 6.16$, $\beta_4 = 26$	18
$AuBr_4^-$	$\beta_4 = 32$	18
$Au(CN)_4^-$	$\beta_4 = 56$	18
$Au(NH_3)_4^{3+}$	$\beta_4 = 30$	18

[a] The symbol k represents the stepwise formation constant, and the symbol β represents the overall formation constant ($\beta_n = k_1k_2...k_n$).

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