Effect of Solution Chemistry on the Extent of Binding of Phenanthrene by a Soil Humic Acid: A Comparison of Dissolved and Clay Bound Humic

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The effect of pH, ionic strength, and cation in solution on the binding of phenanthrene by a soil humic acid in the aqueous phase was determined using fluorescence quenching. The phenanthrene binding coefficient with the dissolved soil humic, \( K_{oc} \), decreased with increasing ionic strength and solution cation valence. At low values of ionic strength, \( K_{oc} \) values for this soil humic acid increased with increasing pH. For this humic sample, the experimental results were consistent with a conformational model of the humic substance in aqueous solution, where, depending on solution conditions, some parts of the humic structure may be more open to allow increased PAH access to attachment sites. After sorption onto clays, supernatant solutions of the unadsorbed humic fraction yielded lower \( K_{oc} \) values than the original bulk humic acid, suggesting that the humic substance was fractionating during its sorption onto the clays. Additionally, the extent of phenanthrene binding with the adsorbed humic fraction was lower than the results determined for the bulk humic acid prior to adsorption. The conformation of the humic substance when sorbed onto the inorganic surface appears to be affecting the level of phenanthrene binding by the humic acid.

Introduction

The transport and partitioning of polycyclic aromatic hydrocarbons (PAHs) as contaminants in groundwater and surface waters are known to be highly dependent on the interaction of these compounds with soil natural organic matter and mobile colloids, which are largely composed of humic substances. In addition, the bioavailability of these contaminants to degrading microorganisms has been closely linked to the sorption capacity of the sediments and organic matter (1, 2). The retardation and migration of the contaminant plume at contaminated sites is calculated from the advection–dispersion equation utilizing a binding coefficient \( K_{oc} \) that estimates the division of the pollutant between the phases. \( K_{oc} \) is defined as the ratio of the concentration of the solute in the solid organic carbon phase to the concentration of the solute in the aqueous phase and is expressed in units of milliliters of solution per gram of organic carbon (mL/g of C). Achieving a better understanding of the causes of the wide variation in experimental values and correlations for the parameter \( K_{oc} \) is an important research goal. \( K_{oc} \) values have even been known to vary spatially within short distances between wells at contaminated site locations. Some potential causes of these variations are the source and origin of the organic matter, the solution chemistry in the groundwater, and the presence of inorganic constituents in the sediments and soils. Several authors have suggested that the binding coefficient of a specific humic substance may be influenced by properties such as its aromaticity, the presence of certain functional groups, or its structure or configuration (3, 4). Some researchers have used \(^{13}\)C NMR information to propose a humic macromolecular model of a large coil with hydrophobic aliphatic sections providing potential binding sites for hydrophobic organic compounds (5). Experiments have been conducted that support the idea of a coiled humic structure that changes its conformation by becoming more expanded at higher values of pH and lower electrolyte concentrations (6–8). Gauthier et al. (9) found a slight increase in \( K_{oc} \) with increasing pH; however, when NaCl was the electrolyte used in experiments between anthracene and soil and aquatic humic acids, but the magnitude of the changes were not reported. Work completed by Schlautman and Morgan (10) evaluated the interaction of three different PAHs with a single humic acid and supported a model of humic material as a void-type structure with specific areas of affinity for hydrophobic solutes, but the trends were not totally consistent for all PAHs studied. Traina et al. (11) studied the complexation of naphthalene with a water-soluble organic carbon solution extracted from a muck soil in the presence of sodium, calcium, and aluminum chloride and found the degree of binding of the PAH to be dependent on the cation species present. The interactions of mixed media complexes (organic humic substances with mineral surfaces) may amend the behavior of the PAH relative to its behavior with each sorbent individually. Humic–mineral complexes may prove to be a very significant source of binding for these contaminants, where the adsorption efficiency depends on the nature and possibly the conformational character of the humic material once it adsorbs to the mineral surface.

The surfaces of metal oxyhydroxides and the edge surfaces of clay particles can react with negatively charged organic acids through a ligand exchange mechanism between the protonated OH\(^{+}\) group and COOH. Sposito (12) proposed the following steps:

\[
\begin{align*}
\text{SOH} + \text{H}^{+} & \leftrightarrow \text{SOH}^{+} \\
\text{SOH}^{+} + \text{Hu}^{+} + \text{COO}^{-} & \leftrightarrow \text{SOH}^{+} \text{COO}^{-} + \text{Hu} \\
\text{SOH}^{+} \text{COO}^{-} + \text{Hu} & \leftrightarrow \text{SOOC}^{+} \text{Hu} + \text{H}_{2}\text{O}
\end{align*}
\]

where SOH represents the surface hydroxyl group on the sorbent, and Hu−COO\(^{−}\) is the humic carboxyl group. Tipping discovered that goethite had twice the capacity for adsorption of humic substances from an aquatic source in the presence of bivalent species than that of a solution containing monovalent cations and anions (13). Murphy et al. (14) found variations in sorption enhancement for humic material sorbed to two different mineral surfaces. The general objective of this work was to evaluate the roles of dissolved bulk natural organic matter (NOM) and mineral-bound NOM in the ultimate distribution and transport of hydrophobic organic compounds.
The research objectives of this study were as follows:

(i) To measure the extent of binding of phenanthrene with a soil humic acid in solution under different conditions of pH, ionic strength, and cation type.

(ii) To determine the influence of the presence of monovalent and multivalent cationic species at different ionic strengths on the extent of soil humic acid sorption onto clay particles of kaolinite and illite.

(iii) To determine if significant fractionation of the humic material onto the inorganic particles is occurring during the sorption process in cation solutions and the extent of its influence on the PAH binding coefficient of the humic coating by comparison to the extent of binding by the dissolved humic acid.

Materials and Methods

API-9 kaolinite and API-35 Fithian illite were obtained from the Wards Natural Science Establishment in Rochester, NY. Project 49 (465) was used to test for the levels of aluminum in solution. The method makes use of the aluminum/morin complex that is measured and referred to a previously prepared calibration curve to determine the aluminum concentration in solution. Total aluminum concentrations in the supernatant were in the range of 0.1 to 0.2 mg/L for 500 g of clay sample. These results demonstrate that maximum of only 1.1 × 10⁻⁶% of the total mass of pure kaolinite [Al₂Si₂O₅(OH)₄] would be dissolved. Similar experiments with the illite sample resulted in higher values of potential clay dissolution but were still only in the range of 6.0 × 10⁻⁹% of the total mass.

The cleaned clay was made homoionic by resuspension in a 0.01 M solution of NaNO₃, Ca(NO₃)₂, or Al(NO₃)₃ for 1 h. Following the resuspension to remove exchangeable cations, the suspension was again centrifuged and the supernatant removed. The water content of the clay pellet resulting from this procedure was evaluated by heating to 100 °C for 12 h and weighing before and after drying. The error introduced from the remaining pore water resulted in an error of less than 1% in subsequent material balance calculations.

The soil humic acid (Reference 1R102H) was acquired from the International Humic Substances Society (IHSS) in Golden, CO. A 100 mg sample was dissolved into 1 L of deionized, distilled, and filtered water with the aid of 3 mL of 0.1 N NaOH. Reported percent elemental analysis from the IHSS results on a dry, ash-free basis are 58.90 C, 3.38 H, 33.46 O, 4.31 N, 0.41 S, and 0.42 P. A concentrated stock solution of phenanthrene was prepared in methanol. Representative microliter quantities of methanol solvent were checked for background fluorescence and found to cause significant interference at the experimental wavelengths used in these experiments. The excitation wavelength/emission wavelength used were 288 nm/364 nm for the phenanthrene probe. NaOH and HNO₃ were used to control pH in experimental stock solutions. NaNO₃ (0.5 M maximum concentration), Ca(NO₃)₂ (0.1 M maximum concentration), and Al(NO₃)₃ (0.01 M maximum concentration at pH 4) were used as background electrolytes. Ionic strengths (I) for the aqueous phase experiments included 0.001, 0.005, and 0.01 M solutions at pH 4, 7, and 10 (aluminum experiments were only done at pH 4 because of solubility limitations). The water used was deionized, distilled, and filtered.

Absorbance measurements were recorded on a Hewlett-Packard model 8452A diode array spectrophotometer to correct for inner filter effect. Fluorescence measurements were performed with a Shimadzu model RF-1501 recording spectrofluorophotometer. Slits were set for 10-nm bandwidths for both excitation and emission monochromators. The analyses of the humic sorption experiments depended upon accurate measurement of total organic carbon (TOC). Glassware was rigorously washed with soap, soaked overnight in 15% HNO₃, and rinsed seven times in distilled water to remove the risk of contamination. TOC was measured on a Shimadzu model TOC-5050A analyzer with an ASI-5000A autosampler. The sorption of humic substance over the course of an experiment occurred over a pH range of 3.9–4.2. pH was measured with a Fisher Acumet pHmeter 25 with an Orion Ross 8103 semi-microcombination electrode. A 0.1-g sample of kaolinite in 25 mL of an experiment provided a surface area of 77.2 m²/L based on BET measurements made in our lab. The same experiment done with illite resulted in a surface area of 268 m²/L. CEC values for these materials were supplied in an API Report for Research Project 49 (17) as 25 mequiv/100 g for the Fithian illite and 6.8 mequiv/100 g for the New Mesa kaolinite.

A clay bound humic experiment was begun by combining the clay and humic suspension in a flask and adding NaNO₃ to increase the ionic strength to 0.001 M and HNO₃ to increase the pH to 4. The suspension was mixed by hand for 1 min, then placed on the shaker table at 300 rpm, and allowed to equilibrate for 4 h. The suspension was centrifuged at 8000 rpm for 30 min, and the supernatant containing the remaining dissolved humic material was decanted and retained. The clay particles were resuspended in fresh electrolyte, shaken for 4 h, and centrifuged again to wash nondesorbed humic acid from the particles. This sequence was repeated for several experiments. No significant desorption of humic material was observed at pH 4 and I = 0.001 or 0.01 M. After these tests, the clay particles were washed only once in subsequent experiments. The humic acid (HA) bound was calculated from the difference between the initial HA concentration as TOC and the final TOC in the equilibrium supernatant solution. The clay particles were resuspended at pH 4 and 1.0 × 0.001 or 0.01 M and spiked with phenanthrene. After being equilibrated, the suspension was centrifuged again (8000 rpm for 30 min) to separate the clay-size material. Evaluations of the kinetics of the sorption process at equilibration times of between 1 and 48 h revealed that after an equilibration time of 4 h no appreciable sorption of phenanthrene was observed (variations were less than the standard error of the fluorescence measurement at ±1.1%).

In contrast to experiments with uncleaned natural particles (18), fast equilibration times (on the order of hours) have been observed by other researchers with fractionated and cleaned inorganic materials (14, 19, 20) and well-characterized humic substances (3, 9–11). Control experiments also indicated no significant loss of phenanthrene to sorption to glass surfaces. PAH concentrations were measured with fluorescence spectroscopy, and the extent of association of phenanthrene with coatings on the different surfaces in the presence of a specific cation was evaluated.

Fluorescence quenching experiments with the bulk humic acid in solution and the supernatant from several experiments were completed to compare the binding by the unadsorbed humic acid fraction to that of the dissolved humic acid before...
adsorption onto the kaolinite surface. Even with its limitations (21), this method still apparently produces more reliable results than some other methods (22). Each Koc value reported in this work indicates the mean value of a series of three to four separate experiments. During each experiment, the extent of binding of phenanthrene was evaluated at six different humic acid concentrations (0–5 mg/L TOC) and analyzed with the Stern–Volmer technique for linear quenching data. Linear regression correlation coefficients were greater than 98% for these data.

A description of the overall process can be summarized in the following simplified steps:

\[
\text{HA + mineral surface} \rightleftharpoons \text{HA}_{\text{residual}} + \text{HA - mineral surface}
\]

\[
\text{HA - mineral surface + PAH} \rightleftharpoons \text{PAH - HA - mineral surface}
\]

\[
\text{HA}_{\text{residual}} + \text{PAH} \rightleftharpoons \text{PAH - HA}_{\text{residual}}
\]

where HA is humic acid, and HA_{residual} is the humic acid remaining in solution after the adsorbed fraction has been removed. In this case, the binding of phenanthrene by the surface-bound HA can depend on the source of the HA, the surface coverage of the HA, and the configuration of the HA on the mineral surface.

Coagulation of the humic acid at the concentrations used in adsorption experiments (5–30 mg/L) at pH 4 was not expected, but with the addition of cation concentrations resulting in ionic strengths of 0.001 and 0.01 M, coagulation and removal of humic material from sedimentation alone was possible. Traina et al. (11) reported visual observations of pinpoint floc with calcium and aluminum solutions mixed with soil humic material at ionic strengths of 0.05–0.5 M. In this study, independent experiments were conducted by mixing the cation solution with humic acid in the absence of the clay particles at I = 0.001 and 0.01 M. No observable floc resulted at I = 0.001 and 0.01 M for the sodium, calcium, and aluminum solutions at pH 4. Absorbance measurements of the humic solutions were checked immediately after mixing and at 5, 15, 30, and 60 min of elapsed time. Within the accuracy of the instrument (±0.005 absorbance units/1% of TOC concentration), no decrease in absorbance resulted for these solutions, suggesting that coagulation and sedimentation of the humic substance was minimal. Additionally, humic solutions of the same pH and ionic strength as those used in the experiments were mixed in Corex tubes, allowed to equilibrate for 12 h, and then centrifuged (8000 rpm for 30 min). No coagulation of humic material was observed based on the lack of a residual solid phase in the tubes.

Material balance of the experimental procedure was evaluated. For a given tube, the mass of phenanthrene remaining in the supernatant solution was determined using fluorescence as a quantitative technique. The residual mass of phenanthrene bound to the humic-coated clay particles was determined through extraction and analysis by capillary gas chromatography with a Hewlett-Packard GC 5890 series II with FID. The clay material remaining in the solid pellet after the supernatant was decanted from the tube was extracted with 1 mL of acetone. The tube with the pellet was sonicated in a water bath for 5 min, shaken at 5-min intervals for 1 h, and allowed to equilibrate for 1 h. After methanol blanks were run to purge the system, standards of 244 and 488 µg/L of phenanthrene in acetone were used to establish a calibration curve at a retention time of 17.33 min. A 10 µL syringe was used to inject a 2 µL sample of the acetone extract from each tube into the capillary GC to measure the response at 17.33 min.

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be used to explain the results for the experiments with the bulk soil humic acid in the aqueous phase used in this study. At low pH, the humic macromolecule adopts a more compact conformation due to the neutralization of the charge—charge repulsion at acidic sites. The more constricted conformation may be the result of the larger molecular weight and size of the humic acid, which is also consistent with such a conceptual model. Other authors that a ligand exchange mechanism of attachment may be suggested (14). The additional affinity of the humic substance for the calcium kaolinite surface in this system may be due to charge neutralization effects of the negatively charged humic acid by attachment with the positively charged cations. As an alternative explanation, a change in humic adsorption mechanism from ligand exchange to water/cation bridging is possible, where the solution cation provides a more direct link between the negatively charged humic with the negatively charged kaolinite edge surface in the attachment process. Theng (24) reported a significant increase in sorption of a fulvic acid onto montmorillonite clay saturated with bivalent cations (including calcium) when compared to sodium and other monovalent cation-saturated montmorillonite.

When a complex mixture such as humic acid is used as the sorbate, some fractionation of the large distribution of complex molecules is expected to occur. To examine this aspect of the adsorption experiments, a computer model called TITRATOR was employed in an attempt to match the experimental adsorption behavior. TITRATOR is a chemical equilibrium simulator that models speciation as a function of pK, pE, or chemical formation constants (25). Using three pseudo-components with artificial formation constants for surface complexation to represent the humic acid, the adsorption data for the attachment of humic acid onto sodium kaolinite was modeled with the results presented in Figure 4. As the material with a higher affinity for the surface is increasingly used up, the second and third pseudo-components begin to contribute more material to the inorganic surface. This result demonstrates how fractionation of the humic substance may occur and still exhibit apparent linear adsorption behavior at low humic concentrations. This explanation is also supported by the desorption results in which the kaolinite was washed in humic-free electrolyte and the humic acid was allowed to desorb. Negligible humic material was desorbed through repeated rinsing (five washes), indicating that the adsorbed material had a strong affinity for the clay surface. In order for desorption to occur, a significant number of contacts (more than five) of humic-

![Figure 3](image3.png)

**FIGURE 3.** Adsorption of soil humic acid onto API kaolinite clay at \( I = 0.001 \text{ M and pH 4.} \)

![Figure 4](image4.png)

**FIGURE 4.** Experimental data for adsorption of soil humic acid onto API kaolinite at \( I = 0.001 \text{ and pH 4 as compared to TITRATOR simulations. Three pseudo-components were used to represent the humic acid with log K values of 1.0, 3.0, and 5.0 for their interaction with a surface species; total surface concentration = 4E-03 M; total HA concentration = 6E-05 M with each pseudo-component having a concentration of 2E-05M.} \)
free water were required to begin to dislodge the adsorbed humic substance. The adsorption of the soil humic acid onto the illite clay surface is presented in Figure 5. On this surface, the humic substance also had a higher affinity for the clay in the presence of the calcium ion than in the presence of sodium.

**Phenanthrene Interaction with Adsorbed Humic Acid.** Once adsorbed onto an inorganic surface, some characteristics of the humic acid, including its ability to bind PAH compounds, may be altered from its original condition in the aqueous phase. The attachment of the PAH to the inorganic clay surface was measured through the use of duplicate blank tubes in each experiment in which the phenanthrene was spiked into a tube with only clay and no humic acid added. Losses of phenanthrene over time to the glass surfaces over time were only 0–0.4% over the time scale of a typical experiment based on blank samples allowed to equilibrate for an equivalent amount of time. The phenanthrene bound to the kaolinite was determined from separate experiments with uncoated clay surfaces and was less than 1% of the available PAH mass in a typical mixed media experiment. That amount was subtracted from the total bound phenanthrene in a mixed media experiment in order to determine the corrected value of $K_{oc}$ determined. Figure 6 is a comparison of the mass ratio of the humic-bound phenanthrene to the phenanthrene in solution versus the amount of organic carbon in the system for both the dissolved bulk humic acid and the kaolinite-sorbed soil humic. The solid line represents the ratio of bound phenanthrene to phenanthrene in solution calculated from the $K_{oc}$ value determined in the dissolved bulk humic acid experiments prior to adsorption onto the clay. The scattered data points indicate the distribution of phenanthrene between the fraction of soil humic acid adsorbed on kaolinite and in solution. The distribution of phenanthrene between the fraction of soil humic acid adsorbed on illite and in solution is presented in Figure 7. In these experiments, the amount of phenanthrene bound by the humic-coated kaolinite was greater in the presence of sodium ion than that in the presence of calcium. $K_{oc}$ values for the humic adsorbed onto the illite were also lower than the $K_{oc}$ values for the dissolved humic acid. However, the scatter of the data in experiments with the illite clay was greater than similar experiments with the API kaolinite. Even though the trends in the data for the adsorbed humic on illite clay were consistent with the earlier results with kaolinite, the interpretation of the data was made difficult by the fact that the illite clay without humic acid had substantial affinity for the phenanthrene (approximately 40% of the phenanthrene in solution in some cases). This was not expected since the illite should be a more highly charged surface than the kaolinite and have even less attraction for the hydrophobic PAH. During the cleaning step with $H_2O_2$, several repetitions of washing resulted in light oily films on the vessel surface and at the air/solution interface. It appears that the cleaning procedure followed may not be effective for a clay of this type. It is likely that this material was not very homogeneous and that residual
organic contamination of the inorganic surface remained even after the washes. Weaver and Pollard (26) also found this clay material to have significant inhomogeneity.

In this study, the adsorption of soil humic acid to kaolinite and illite clays followed a Langmuir-type isotherm in which a plateau or adsorption maximum was achieved that has been observed by other investigators using cleaned inorganic surfaces (14, 13, 19, 23). Assuming that this plateau was an approximation for monolayer saturation onto the clay surfaces, a model was applied in which the fractional coverage of humic adsorption onto the inorganic surface was estimated based on the mass ratio of the experimentally determined adsorbed TOC and the saturation estimate. The limitations of this approach includes the assumptions of monolayer coverage and that the molecular areal coverage by a single humic macromolecule remains approximately the same. Murphy et al. (19) produced high-performance size exclusion chromatographic results for a peat humic acid which demonstrated that at a given pH and ionic strength the relative size of the humic should remain approximately the same for a specific background electrolyte. However, the peaks were different when calcium or sodium solutions were used. Cornel et al. (7) also presented hydrodynamic radii results for a humic substance in which changes in pH and ionic strength were required to affect the relative Stokes–Einstein radius for the humic acid.

When both organic and inorganic surfaces are present, a summation model of the mineral and organic contributions to sorption has been proposed (27):

$$K_d = f_{oc \text{ adsorbed}} K_{oc \text{ adsorbed}} + f_i K_i$$  

where $K_d$ is the overall distribution coefficient for both the mineral and organic components (mL/g), $f_i$ is the fraction of mineral surface area available for PAH sorption, $K_i$ is the surface area-normalized distribution coefficient for the inorganic component (mL/cm$^2$), $K_{oc \text{ adsorbed}}$ and $f_{oc \text{ adsorbed}}$ refer to the adsorbed humic acid, and $S_i$ is the sorbent surface area (cm$^2$/g). In this study, independent measurements of the inorganic surface adsorption coefficient were made, and the overall equilibrium distribution value was also measured experimentally. If the fractional coverage of the surface by humic material is estimated, the effective $K_{oc \text{ adsorbed}}$ for phenanthrene can be evaluated and compared with other observations.

For several series of experiments, the supernatant from adsorption experiments was retained and used to evaluate the binding coefficients for the unadsorbed humic fraction. Since the humic material is a mixture of complex macromolecules, some fractionation for some of the material is reasonable. For example, the larger molecular weight humic acid particles may preferentially adsorb to the inorganic surface, which results in the material attached to the surface not being the same as the original bulk humic acid and therefore also different from the humic substance remaining in solution. For this study, the important aspect of this characteristic is whether the fractionation affects the PAH binding capacity of the humic acid. One approach is the treatment of the humic substance as if it were a mixture of two broad groups of material. In that case, the overall PAH binding capacity of the dissolved humic acid would be proportioned among the two phases:

$$K_{oc \text{ adsorbed/HA}} = f_{oc \text{ adsorbed}} K_{oc \text{ adsorbed}} + f_{oc \text{ residual}} K_{oc \text{ residual}}$$

where $K_{oc \text{ adsorbed/HA}}$ is the binding coefficient of the bulk humic acid in the aqueous phase prior to adsorption, $f_{oc \text{ adsorbed}}$ is the fraction of organic carbon absorbed to the surface, $K_{oc \text{ adsorbed}}$ is the binding coefficient calculated for the adsorbed humic fraction, $f_{oc \text{ residual}}$ is the fraction of organic carbon remaining in the supernatant solution after adsorption, and $K_{oc \text{ residual}}$ is the binding coefficient for the supernatant solution.

To perform this evaluation, the binding coefficient of the residual supernatant solution of the humic material after adsorption was determined. Experiments to perform this calculation were completed to include separate absorbance and background fluorescence measurements to enable $K_{oc}$ determinations for these solutions using the fluorescence quenching technique. The results of these experiments at pH 4 and $I = 0.001$ M are presented in Table 1. The column on the left lists the experimental results for the dissolved humic acid before adsorption onto the clay surface. The right-hand column describes $K_{oc}$ results from experiments with the centrifuged supernatant from the experiments in which the humic acid is adsorbed onto the clay. The mean $K_{oc}$ value for the experiments in which sodium was the background electrolyte was significantly higher than the experiments with calcium ($p = 0.051314$). The mean $K_{oc}$ for the experiments with the residual humic acid supernatant from the adsorption experiments was lower than that of the experiments with the bulk dissolved humic acid in both the case of the sodium solution ($p = 0.002728$) and the calcium solution ($p = 0.000414$). In both cases the corresponding extent of binding of PAH by the dissolved bulk humic acid was greater than the binding by the mineral bound humic.

The comparison of the calculations for $K_{oc \text{ adsorbed}}$ from the two models using eqs 1 and 2 at pH 4 and $I = 0.001$ M are presented in Table 2. The mean of the experimental calculations for $K_{oc \text{ adsorbed}}$ in sodium solution from model 1 (called the summation model [SM]) is $4.45 \pm 0.56 \times 10^4$ and $2.51 \pm 0.16 \times 10^4$ mL/g in calcium solution. Calculations from model 2 (called the two phase model [TPM]) yielded $K_{oc \text{ adsorbed}}$ of $3.34 \pm 0.101 \times 10^4$ mL/g in sodium solution and $2.24 \pm 0.59 \times 10^4$ mL/g in calcium solution. In the cases of both solutions, the TPM estimated a significantly lower $K_{oc \text{ adsorbed}}$ than the SM model. Also, for both sets of experiments, the $K_{oc \text{ adsorbed}}$ values for the calcium experiments were lower than those from

<table>
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<tr>
<th>Cation in Solution</th>
<th>$K_{oc}$ Values for Dissolved Humic Acid</th>
<th>$K_{oc}$ Values for HA Supernatant after Adsorption Expt</th>
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<tr>
<td>Sodium</td>
<td>Mean 3.33, SD 0.550, $p$ value 0.02728</td>
<td>Mean 2.36, SD 0.269, $p$ value 0.00414</td>
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<tr>
<td>Calcium</td>
<td>Mean 2.33, SD 0.300, $p$ value 0.051314</td>
<td>Mean 1.92, SD 0.139, $p$ value 0.000414</td>
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*Experiments at pH 4 and $I = 0.001$ M; adsorption onto kaolinite clay.*

*TABLE 1. Summary of Binding Coefficient Results for Dissolved Humic Acid and Supernatant from Adsorption Experiments*
TABLE 2. Comparison of Results for Calculated $K_{oc}$ for Humic Acid Adsorbed onto Kaolinite from Two Models $K_{oc}$
($\times 10^{-4}$ mL/g of C)

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<tr>
<th>cation in solution</th>
<th>K$_{oc}$ values</th>
<th>K$_{oc}$ values</th>
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<td>2.52</td>
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mean 4.45 mean 3.34 mean 2.51 mean 2.24
SD 0.56     SD 1.01     SD 0.16     SD 0.59

FIGURE 8. Predicted $K_{oc}$ values (based on the difference between measured $K_{oc}$ for residual soil humic acid and the bulk soil humic acid in aqueous solution prior to adsorption) compared to experimental values for adsorbed soil humic acid on API kaolinite at $I = 0.001$ M and pH 4.

identical experiments conducted in the presence of sodium electrolyte and sodium kaolinite.

Another way to represent these findings for the humic acid/kaolinite system is presented as Figure 8. In this case, the calculated $K_{oc}$ for each experiment is plotted versus the mass of organic carbon in the system. The solid lines represent the $K_{oc}$ from experiments with the unadsorbed bulk humic acid, and the dashed lines show the predicted $K_{oc}$ based on the SM model. In almost every case, the actual $K_{oc}$ for the adsorbed humic acid is much less than the predicted $K_{oc}$ based on fractionation of the humic material, especially at high surface coverages. The actual adsorbed $K_{oc}$ values are also less than the $K_{oc}$ for the bulk humic acid prior to adsorption. Since the $K_{oc}$ predicted by the SM model represents the hypothetical binding by the adsorbed humic acid fraction as if it were in aqueous solution, the conclusion is that something other than humic fractionation differences are needed to explain the observed trends. On the basis of fractionation considerations alone, the expected result is that the binding of phenanthrene by the adsorbed humic acid should be higher than the bulk humic acid prior to adsorption. These data suggest that the surface conformations of the humic acid may be having a significant influence on its PAH binding characteristics.

The results from the material balance experiments are presented in Table 3. Overall material balance results were within the range expected for experiments of this type (23), which provides some assurance that compound losses to other surfaces or volatilization were not significant. An unexpected but important observation from examination of the data was a significant difference in the overall recoveries from the humic coatings made in the presence of sodium when compared to the coatings from the calcium experiments. The mean recovery of phenanthrene was 86.6% (SD 8.5%) for the sodium experiments and 106.8% (SD 2.7%) for the experiments with the calcium clay. The difference between these two sets of experiments was found to be significant ($p$ value = 0.00491). The cause of the decrease in the efficiency of the extraction procedure for the sodium organic complex remains speculative; however, a more open configuration of the humic substance could allow for a stronger attachment into a larger void in the humic structure. This could reduce the efficiency of the extracting fluid.

In some cases, the mass fraction of organic carbon adsorbed onto the clay surface was less than others. The material with the strongest affinity for the inorganic surface may be adsorbing preferentially, leaving a different distribution of material in solution than that on the surface. However, the effect of this change in distribution on the determination of $K_{oc}$ is not clear. A comparison of results for only those experiments in which the fraction of organic carbon adsorbed ranged from 47 to 53% was made. When restricted to only those results, the difference between the $K_{oc}$ calculated from the SM model for the sodium experiments (4.28 ($\pm 0.13$) $\times 10^{4}$ mL/g for six observations) and the calcium experiments (2.69 ($\pm 0.07$) $\times 10^{4}$ mL/g for seven observations) was still significant ($p$ value = $10^{-11}$). The results indicate that the trend in the difference between the calcium experiments and sodium experiments remain consistent for those cases in which similar mass fractions of organic carbon are adsorbed. However, the molecular weight and functional

TABLE 3. Experimental Material Balance Evaluation for Phenanthrene/Soil Humic/Kaolinite System

<table>
<thead>
<tr>
<th>mass of phenanthrene in supernatant (µg)</th>
<th>mass of phenanthrene extracted from adsorbed humic (µg)</th>
<th>overall mass balance % recovery of total spike</th>
</tr>
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<tr>
<td>sodium</td>
<td>0.674</td>
<td>93.1</td>
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<td>0.690</td>
<td>91.9</td>
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<td></td>
<td>0.582</td>
<td>74.4</td>
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<td>mean</td>
<td>0.625</td>
<td>mean 351</td>
</tr>
<tr>
<td>SD</td>
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<td>SD 8.5</td>
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<tr>
<td>calcium</td>
<td>0.736</td>
<td>110.4</td>
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<tr>
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<tr>
<td>mean</td>
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<tr>
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<td>0.02</td>
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<td>$p$ value</td>
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$^a$ Experiments at pH 4 and $I = 0.001$ M ionic strength.
group distributions of the two humic fractions may still be different.

The configuration of the adsorbed humic substance on the inorganic surface can depend on the surface density and distribution of the surface reactive sites present on the inorganic surface and the structure and conformation of the humic substance due to the number of attachment sites and the degree of ionization of carboxylic and phenolic groups on the humic material. This could potentially explain the lower Koc values for the adsorbed humic acid when compared to the bulk humic in solution. Some important limitations of this study are that only one humic substance was evaluated, that the type of distribution of humic material was assumed to be the same in solution as that adsorbed onto the surface, and that the method of estimating the fractional coverage of clay surface by the organic matter in the first model is only an approximation. Nevertheless, some interesting comparisons can be made from the results. In the presence of calcium and sodium electrolyte, the distribution coefficient for phenanthrene associated with a soil humic acid adsorbed onto kaolinite was less than the distribution coefficient for phenanthrene with the bulk dissolved humic acid. This result suggests a change in the conformation of the humic upon adsorption in which some binding sites become inaccessible to the phenanthrene probe. In addition, the distribution coefficient for the phenanthrene attached to the sorbed humic acid in the presence of sodium was higher than that in calcium electrolyte. In the calcium solution, the clay-bound humic acid may adopt a more condensed conformation in which additional cation bridging between functional groups combines to form a more compact structure, reducing the accessibility of phenanthrene binding sites. Two models have been evaluated in which a physical description of the system can result in calculations for adsorbed Koc values that qualitatively predict the differences observed in the experimentally observed binding results. Further work is needed to better characterize the molecular weight distribution and functional grouping of an adsorbed humic mixture and to compare those results with that of the residual humic substance remaining in solution.

Literature Cited

(7) Cornel, P. R.; Summers, R. S.; Roberts, P. V. J. Collid Interface Sci. 1988, 110, 140.