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Pyrene Sorption by Water-Soluble Organic Carbon

Bruce E. Herbert

Department of Geology, Texas A&M University, College Station, Texas 77843

Paul M. Bertsch*

Division of Biogeochemistry, Savannah River Ecology Laboratory, University of Georgia, Aiken, South Carolina 29802

Jeff M. Novak

Division of Biogeochemistry, Savannah River Ecology Laboratory, University of Georgia, Aiken, South Carolina 29802

■ Natural dissolved organic matter (DOM) in soil solution has the potential to facilitate the transport of nonionic organic contaminants (NOC). The interactions between pyrene and ultrafiltration fractions of water-soluble organic carbon (WSOC), humic acid, and fulvic acid were quantified using fluorescence-quenching spectroscopy. Pyrene partition coefficients to the smaller WSOC fractions varied between 4.1×1.0^3 and 6.8×10^3 L kg^{-1}, while partition coefficients for the largest fraction of WSOC, humic acid, and fulvic acid were 1.5×10^4, 1.7×10^5, and 1.1×10^4 L kg^{-1}, respectively. These results demonstrate that the use of the same $^cK_{oc}$ value to describe NOC partitioning to both immobile organic matter and soil solution DOM will overestimate the ability of DOM to facilitate the transport of NOC. Conversely, pyrene partitioning data to the largest WSOC fraction suggest that the presence of colloidal organic matter suspended in the soil solution may have a large influence on NOC transport.

Introduction

The potential for the facilitated transport of nonionic organic contaminants (NOC) through the vadose zone via association with mobile colloidal particles and natural organic macromolecules has recently been acknowledged (*1–3*). Models of colloidal transport conceptualize the vadose zone as a three-phase system where the contaminant partitions between the immobile solid matrix, the mobile aqueous phase, and the mobile colloids. Natural organic matter, present as dissolved macromolecules, organic particulates, and coatings on inorganic colloids such as clay and iron oxide particles, comprises the most important material in soil solutions capable of facilitating the transport of NOC. The overall influence of these natural carriers on NOC transport is dependent on their concentration in soil solution, the degree of their interaction with the organic contaminant, their stability as suspensions, and their mobility through the vadose zone (*2*).

The composition of mobile carriers in soil solution has been assumed to be chemically similar to the immobile phase, and therefore, NOC partitioning to the two phases should also be similar (*2*). This assumption may not be accurate for soil systems where dissolved organic matter (DOM) is the major mobile carrier. This is due to differences between the chemical characteristics of DOM in soil solution and bulk soil organic matter, leading to differences in observed NOC sorption coefficients. Alkali-extracted soil organic matter and commercially available humic acids have been extensively used as models of natural DOM (*4–7*). These studies have typically shown strong interactions between NOC and the model DOM. Recent work has focused on the characterization of natural organic matter extracted from soils with water or aqueous salt solutions and NOC sorption to this material (*8–11*). This material, defined as water-soluble organic carbon (WSOC), is presumed to better represent soil solution DOM compared to base-extracted organic matter. Use of WSOC to quantify NOC sorption to soil solution DOM may provide more realistic estimates of organic contaminant sorption in three-phase systems.

This study is based on the hypothesis that the chemical characteristics of soil solution DOM, as represented by WSOC, are distinct from the characteristics of base-extracted humic and fulvic acids. Because of these differences, results from experiments designed to estimate the ability of soil solution DOM to facilitate the transport of NOC will be influenced by the type of organic carbon used as a model for DOM. We have examined the interaction between pyrene, a polycyclic aromatic hydrocarbon on the USEPA priority pollutant list, and several types of natural DOM, using fluorescence quenching. Equilibrium fluorescence quenching is a noninvasive technique that has been used to quantify conditional organic carbon sorption coefficients for several fluorescent compounds, including polycyclic aromatic hydrocarbons (PAH) (*4, 9, 10*). The specific objectives of this investigation were (i) to chemically characterize WSOC, (ii) to quantify the degree of interaction between pyrene and WSOC, and (iii) to compare the chemical characteristics and sorption of pyrene to WSOC and base-extracted humic and fulvic acids.

Experimental Section

Materials. Aqueous solutions of pyrene (Aldrich, 99%, used as received) were made by shaking an excess of the solid in solutions adjusted to pH 5 with HCl and 0.01 M ionic strength with $NaClO_4$. The solutions were shaken for 24 h at 298 K, passed through a 0.2-μm polycarbonate filter to remove excess solid pyrene, and stored at 277 K. Acridine orange (EM Science, Cherry Hill, NJ) was dissolved in distilled, deionized water (DD H_2O) to give a final concentration of 1 mg L^{-1} and stored at 277 K. Pyrene and acridine orange solutions were prepared and stored in amber borosilicate jars with Teflon-lined lids. Fluorescence-quenching experiments were conducted in 11.1-mL glass vials with Teflon-lined caps. All glassware used in these experiments was washed with detergent, rinsed with DD H_2O, and finally solvent-rinsed with a methanol, hexane, and methanol sequence.

Natural organic matter was extracted from the 0–10-cm depth of a Pickney soil (Cumulic Humaquept, Aiken County, SC) that was sieved field-moist through a 2-mm sieve. To extract WSOC, 150-g samples of soil were placed in 250-mL polypropylene bottles with 150 mL of DD H_2O. The bottles were shaken for 3 h at 298 K and then centrifuged at 3400*g* for 45 min. The supernatant was successively filtered through Whatman No. 42 and 0.4-mm polycarbonate filters that were prerinsed with DD H_2O. The resulting organic carbon solution had a DOC concentration of approximately 40 mg L^{-1} and was stored in glass at 277 K. Humic and fulvic acids were extracted from the same soil using a modified method from Schnitzer (*12*). After extraction under argon with 0.1 M NaOH, the humic

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material was repeatedly fractionated with 6 M HCl and 2 M NaOH under argon. The humic acid was purified with an 0.1 M HCl and 0.3 M HF treatment, dialyzed in tubing of 1000 nominal molecular weight cutoff (NMWCO) against DD H_2O, and freeze-dried. The fulvic acid solutions were purified by repeated passage through a H^+-saturated cation-exchange column and evaporated to dryness at 313 K. Solutions of humic and fulvic acids used in the fluorescence-quenching experiments were made by adding the organic matter to a 0.01 M $NaClO_4$ solution adjusted to pH 8 with NaOH and then sonicated until dissolved.

WSOC Fractionation. A modified concentration technique (*13*), using Amicon stirred ultrafiltration cells (Amicon Division, W. R. Grace and Co., Beverly MA), was used to size-fractionate the WSOC. Cascade ultrafiltration, through 100 000, 30 000, 10 000, and 1000 nominal molecular weight cutoff filters, was used to fractionate the WSOC. Four retentate fractions, labeled WSOC-R1, WSOC-R2, WSOC-R3, and WSOC-R4, resulted. As the solutions were filtered, WSOC concentrations within the cells increased, to a point where the concentration of DOM in the filtrate rapidly increased. This is attributed to a decrease in size due to a change in conformation of the large molecular weight organic molecules, as DOM concentration increases (*13*). This breakthrough of DOM was monitored by UV absorbance at 290 nm. Once breakthrough was detected, DD H_2O was added to the cell to decrease WSOC concentrations within the cells and minimize breakthrough. Filtration was continued until a second breakthrough event occurred, at which time collection of filtrate was ceased. Filtration was then continued until the volume of retentate within the ultrafiltration cell was less than 1 mL, without collection of the filtrate. The retained organic carbon was then washed from the membrane filter with water adjusted to pH 8 with NaOH. Resulting retentate DOC concentrations were approximately 70–80 mg L^{-1}. Each WSOC fraction was placed in 1000 NMWCO dialysis tubing and then dialyzed against Na^+-saturated Chelex 100 resin (Bio Rad, Richmond, CA) for 48 h. Organic carbon concentrations in the solutions were then measured, and the material was stored in glass at 277 K. Organic carbon concentrations were measured with a Shimadzu TOC-500 organic carbon analyzer using dextrose standards made with HPLC grade water. Contamination by the Chelex resin and dialysis tubing was minimized by washing these materials according to manufacturer's instructions and rinsing with DD H_2O. Blanks were analyzed for DOC concentration to confirm the lack of contamination.

Organic Carbon Characterization. Total acidity was operationally defined as the amount of base consumed per amount of H^+-saturated organic carbon during a direct titration to pH 10. Total acidity of natural organic matter is usually measured by an indirect titration using barium hydroxide (*14*). This technique is appropriate if all DOM can be separated from the barium hydroxide before the final titration. Because unfractionated WSOC may contain appreciable amounts of small molecular weight organics that are inseparable from the barium hydroxide, a direct titration was chosen to measure total acidity (*13*). Stepped titrations of the organic matter solutions were performed under argon and at 293 K, with CO_2-free NaOH, which had been standardized with potassium acid phthalate (KHP). WSOC size fractions were passed through H^+-saturated cation-exchange columns (Dowex 50W-X8, Bio Rad, Richmond, CA) until the solution pH and electrical conductivity were constant. The ionic strength of the WSOC fractions was adjusted to 0.1 M with $NaClO_4$, while the humic and fulvic acids were adjusted to 0.005 M with KCl. Titrations were corrected for solution blanks. Direct titrations of the organic carbon fractions were made with a Radiometer TTT8890 titrator (Radiometer A/S, Copenhagen, Denmark), with a PHM84 pH meter and ABU80 autoburet.

The relative hydrophobicity of the WSOC fractions, fulvic acid, and humic acid was accessed using reversed-phase chromatography. Using a concept similar to the DOM fractionation technique developed by Leenheer (*15*), C-18 reversed-phase columns (Seppaks, Waters, Milford, MA) were used to separate DOM into operationally defined hydrophobic and hydrophilic fractions. Each Seppak was pretreated with 20 mL of methanol and rinsed twice with 20 mL of DD H_2O before use (*16*). Blanks were processed by passing 5 mL of DD H_2O through the Seppak. The DOM solution was then acidified to pH 2 with H_3PO_4 and passed through the pretreated Seppak. After 5 mL of the DOM solution had eluted from the Seppak, 2 mL of the DOM sample was collected for analysis of the dissolved organic carbon (DOC) concentration. The hydrophobic fraction (H), as a function of total DOC, was calculated as

$$H = \frac{([DOC_i] - ([DOC_u] - [DOC_b]))}{[DOC_i]} \times 100 \qquad (1)$$

where $[DOC_i]$, $[DOC_u]$, and $[DOC_b]$ are the initial, unretained, and blank DOC concentrations, respectively. The advantages of using solid-phase extraction to fractionate DOM are its ease of operation and relatively low amounts of leachable organic contaminants in the extraction cartridges.

Fluorescence Quenching. Fluorescence measurements were made on a Shimadzu RF5000 fluorometer (Shimadzu Crop., Kyoto, Japan) with excitation and emission slit widths of 5 nm. Excitation and emission wavelengths were 332 (ex) and 374 nm (em) for pyrene and 262 (ex) and 521.6 nm (em) for acridine orange. Absorbance measurements of the dissolved organic matter solutions were made with a Shimadzu 2100U UV spectrophotometer.

Stock solutions of pyrene, DOM, and DD H_2O were adjusted to pH 5 and 0.01 M ionic strength with NaOH, HCl, and $NaClO_4$, respectively. Preliminary experiments indicated that significant amounts of pyrene adsorbed to the glass walls of the vials during the fluorescence-quenching experiments. To quantify pyrene adsorption to glass, 0–3 mL of pyrene solution was combined with the $NaClO_4$ solution to give a total volume of 10 mL in the 11.1-mL vials. The vials were then shaken for 24 h at 295 K, at which time the pyrene fluorescence was measured in preequilibrated quartz cuvettes. To measure pyrene fluorescence in the absence of adsorption to glass (F_0) at the same pyrene concentrations as those used above, 0–1 mL of pyrene stock solution was combined with 0–2 mL of $NaClO_4$ solution to give a total of 3-mL volume in a stirred cuvette. The cell was equilibrated with this solution for 15 min, after which time a new solution of the same concentration was prepared in the cuvette and immediately placed in the fluorometer, and the fluorescence was measured. The fluorescence of acridine orange solution, assumed to have a stable fluorescence, was measured in a separate cuvette and used to correct for instrument drift.

The quenching of pyrene fluorescence, resulting from its partitioning to DOM, was determined by combining 2 mL of pyrene, 0–3 mL of the DOM stock solutions of known concentration, and 5–8 mL of $NaClO_4$ solution

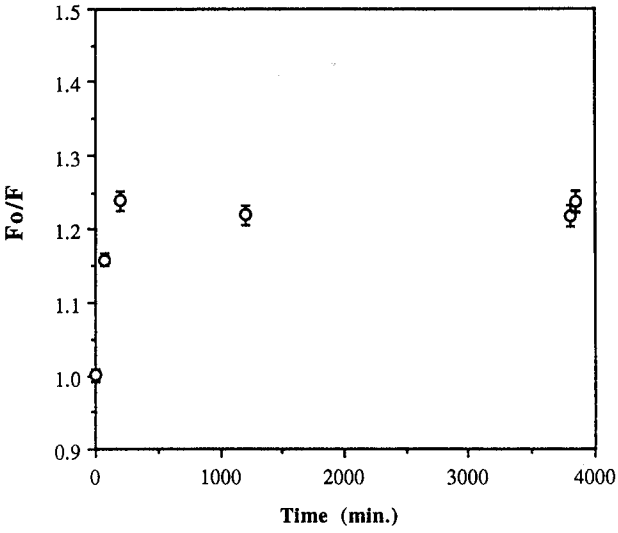

Figure 1. Kinetics of pyrene sorption to unfractionated WSOC.

(10.0-mL total volume) in glass vials. Three replicate solutions at eight DOC concentrations were prepared for each of the WSOC fractions used in this study. The quenching of pyrene by humic acid and fulvic acid was quantified using three replicate solutions at six concentrations. An evaluation of the kinetics of pyrene partitioning to unfractionated WSOC was done to determine an adequate equilibration time for the pyrene-quenching experiments (Figure 1). The partitioning of pyrene to WSOC was observed to be complete within 4 h; therefore, an equilibrium time of 24 h was deemed to be adequate for these reactions. The vials were then shaken at 295 K for 24 h, and the fluorescence was measured in preequilibrated quartz cuvettes. The range of DOC concentrations was 0–40 mg L^{-1}. DOM solutions, without pyrene, were prepared at the same concentrations as used in the quenching experiments. The UV absorbance and fluoresence at the excitation and emission wavelengths of pyrene were measured on these solutions to allow correction for the inner filter effect and the intrinsic fluorescence contributed by the DOM, respectively (*4*). Fluorescence in the absence of DOM or adsorption to the glass wall (i.e., F_o) and instrument drift were measured as previously described.

Data Analysis. Assuming that the fluorescent lifetime of the fluorophore can be modeled as a single exponential, the linear Stern–Volmer equation relates the decrease in fluorescence to quencher concentration (*4, 17*)

$$F_0/F = 1 + {}^cK_{oc}[\mathrm{OC}] \quad (2)$$

where F_0 is the fluorescence in the absence of DOM, F is the fluorescence in the presence of quencher at various concentrations, ${}^cK_{oc}$ is the partition coefficient, and [OC] is the organic carbon concentration of the WSOC, fulvic acid, or humic acid solution. Derivation of this equation is based on a number of assumptions. Use of this equation assumes that loss of fluorescence by any other mechanism, such as adsorption to glassware, is insignificant, that fluorescence intensity is proportional to the free fluorophore concentration, and that quenching occurs primarily by a static mechanism (*4*).

As stated previously, significant pyrene adsorption to glassware was observed in preliminary experiments. The equilibrium glass adsorption coefficient, K_w, is defined as

$$K_w = [\text{Py-wall}]/[\text{Py}] \quad (3)$$

where K_w is the conditional adsorption coefficient, [Py-wall] is the mass of adsorbed pyrene per unit volume of sample, and [Py] is the concentration of the dissolved pyrene. Using the pyrene mass balance and the assumption that adsorbed pyrene is nonfluorescent, the loss of fluorescence is related to K_w by

$$F_0 - F = (S/V)K_wF \quad (4)$$

where F_0 is the fluorescence intensity in the absence of adsorption to glass and F is the intensity after adsorptive loss. F_0 and F are related to the total and free PAH concentrations, respectively. A plot of $F_0 - F$ versus F gives a slope equal to $(S/V)K_w$. Combining the linear Stern–Volmer equation (eq 2), along with the expression for K_w (eq 4), gives the expression

$$F_0/F = 1 + (S/V)K_w + {}^cK_{oc}[\mathrm{OC}] \quad (5)$$

Plots of F_0/F versus [OC] give a slope of ${}^cK_{oc}$ and an intercept of $1 + (S/V)K_w$.

Table I. Chemical Characteristics of WSOC and Base-Extracted Humic and Fulvic Acids Used in This Study[a]

sample	NMWCO[b]	acidity, equiv kg^{-1} OC	H, %
WSOC[c]	NA[d]	14.9 (0.31)	8.6 (1.0)
WSOC-R1	100000	ND[e]	23.8 (3.4)
WSOC-R2	30000	4.47 (0.04)	7.7 (0.8)
WSOC-R3	10000	7.95 (1.00)	18.4 (1.4)
WSOC-R4	1000	7.93 (0.64)	22.2 (0.4)
humic acid	NA	12.1 (0.79)	75.3 (6.5)
fulvic acid	NA	19.5 (0.34)	34.4 (0.5)

[a] Standard errors are in parentheses. [b] Nominal molecular weight cutoff. [c] Unfractionated WSOC. [d] Not applicable. [e] Not determined.

Results and Discussion

Organic Carbon Characterization. The total acidities of the WSOC fractions, WSOC-R2, WSOC-R3, and WSOC-R4, were significantly lower ($\alpha = 0.05$) than the humic and fulvic acids and the unfractionated WSOC (Table I). The acidities of these fractions were lower than the reported total acidities for aquatic and soil humic substances, which average 10–16 (*18*) and 12–24 equiv kg^{-1} C (*19*), respectively. The lower acidities of the WSOC fractions may reflect the presence of a higher proportion of nonacidic, water-soluble, nonhumic organic compounds derived from plant leachates. Low acidities of humics extracted from soil solution DOM have also been attributed to the presence of plant leachates (*20*). ^{13}C NMR spectroscopy has shown that WSOC contains higher proportions of nonacidic polysaccharides and other similar compounds derived from plant leachates, compared to fulvic and humic acids (*21, 22*). In contrast to the size-fractionated WSOC, the high total acidity of the unfractionated WSOC implies that this material probably contains a significant amount of simple organic acids, compounds that would not have been retained with the fractionated WSOC because of their small molecular size.

The proportion of an operationally defined hydrophobic fraction to total DOM has often been related to its movement in soil and its interaction with NOC (*23–25*). The hydrophobic fraction, H, varied for the different WSOC fractions, and the humic and fulvic acids. The H of the WSOC fractions were significantly lower ($\alpha = 0.05$) than those of humic and fulvic acids, ranging from 8% to 24% of total DOM. Though H was not correlated with the nominal molecular weights of the WSOC fractions, the largest fraction, WSOC-R1, exhibited the largest H. The hypothesis that WSOC contains higher proportions of nonhumic organic compounds is consistent with the observed differences in hydrophobic content between humic

Table II. Fitted Stern–Volmer Parameters for Pyrene Quenching to WSOC and Humic and Fulvic Acids[a]

sample	slope	intercept	R^2	$^cK_{oc}$, L kg^{-1}
WSOC[b]	4.05×10^{-3} (0.32)	1.02 (0.005)	89	4.05×10^3
WSOC-R1	1.54×10^{-4} (1.7)	1.03 (0.006)	80	1.54×10^4
WSOC-R2	4.53×10^{-3} (0.18)	1.02 (0.004)	97	4.53×10^3
WSOC-R3	6.75×10^{-3} (0.48)	1.03 (0.005)	90	6.75×10^3
WSOC-R4	4.10×10^{-3} (0.25)	1.02 (0.005)	93	4.10×10^3
humic acid	1.70×10^{-5} (9.9)	1.09 (0.03)	95	1.70×10^5
fulvic acid	1.07×10^{-4} (1.6)	1.10 (0.007)	72	1.07×10^4

[a] Standard errors are in parentheses. [b] Unfractionated WSOC.

and fulvic acids and WSOC. As the technique was used in this study, the fraction of DOM retained by solid-phase extraction should correspond most closely with the hydrophobic acids and neutrals retained on XAD-8 resin using the fractionation technique of Leenheer (*17, 26–28*). Solid-phase extraction has the potential for rapid characterization of the relative hydrophobicity of DOM, especially under field conditions. This technique is currently being evaluated by the authors.

Soil organic matter is a complex mixture of humic and nonhumic organic compounds. The chemical characteristics of the WSOC and base-extracted humic and fulvic acid fractions are dependent on the subsample of total soil organic matter extracted by the particular extraction technique. Except for the high acidity of the unfractionated WSOC, fractionated WSOC was less charged and less hydrophobic than the base-extracted humics. The higher proportion of larger molecular weight polyelectrolytes in the base-extracted materials increases both their acidity and hydrophobicity as compared to the WSOC fractions. Two conclusions can be drawn from these characterization studies. First, the chemical characteristics of soil solution DOM are distinct from those of base-extracted humic and fulvic acids. Second, soil solution DOM may have greater mobility in the soil environment than base-extracted humics because of its lower hydrophobicity.

Fluorescence Quenching. Fluorescence quenching is described with a linear Stern–Volmer plot that relates the decrease in fluorescence to quencher concentration through the Stern–Volmer quenching constant, using the assumption that fluorescence intensity is proportional to the free fluorophore concentration (*4*). If a static quenching mechanism is assumed, i.e., where a ground-state association between DOM and the fluorophore quenches the fluorescence, then the quenching constant corresponds to the conditional sorption coefficient. Recently several of the assumptions underlying this approach have been questioned (*10, 29*). Backhus and Gschwend (*10*) have extended the Stern–Volmer equation to include the case where the total fluorescence is proportional to the free fluorophore concentration and a fraction of the bound fluorophore, though the authors assumed that humics fully quenched fluorophores. In another study, Morra et al. (*29*) examined both fluorescence quenching and fluorescence lifetimes of naphthalene in humic acid solutions and found that both dynamic and static mechanisms were contributing to the observed quenching; however, the influence of the dynamic mechanism on the observed quenching appeared to be small in this study (*29*). In general, fluorescence quenching and other techniques of quantifying $^cK_{oc}$ result in $^cK_{oc}$ values which are in reasonable agreement (*4, 10*).

Pyrene sorption to the glass walls of the vials exhibited a linear isotherm. Using eq 4, K_w was calculated to be 9.6 $\times 10^{-4}$ mL cm^{-2}. Using the calculated values of K_w, S, and V, the intercept of the Stern–Volmer plots for pyrene was

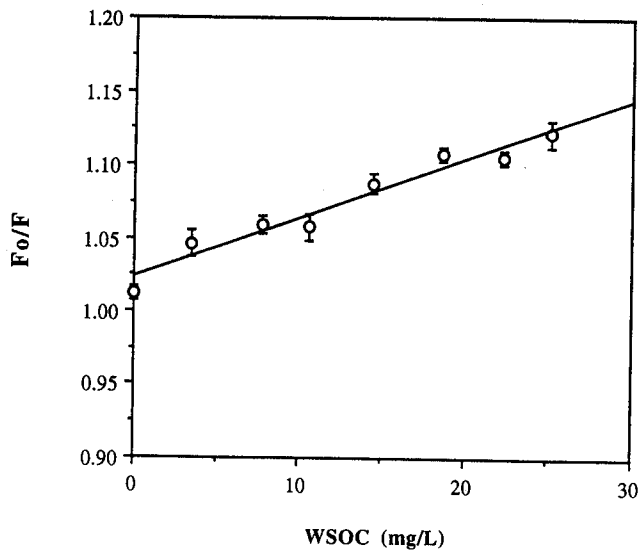

Figure 2. Stern–Volmer plot of pyrene quenching by unfractionated WSOC.

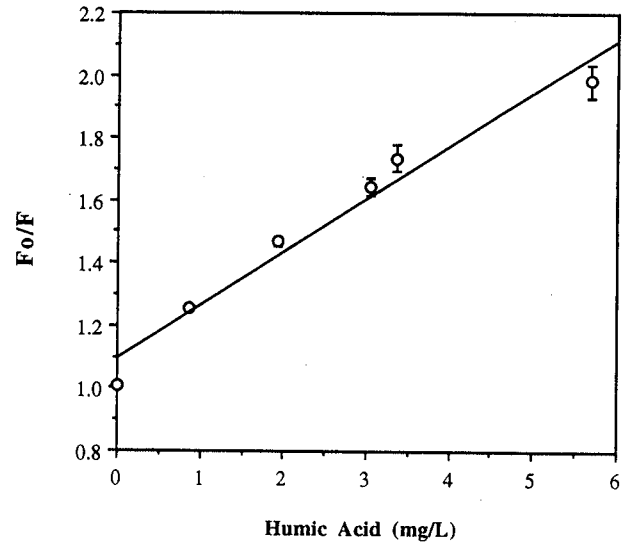

Figure 3. Stern–Volmer plot of pyrene quenching by humic acid.

determined to be 1.03. This value is within the 95% confidence interval of the intercept values calculated from the linear regressions of the pyrene-quenching data for all samples except for humic acid (Table II), supporting the use of K_w.

The linear Stern–Volmer plots of pyrene quenching by unfractionated WSOC and humic acid are given in Figures 2 and 3. Plotted data points represent mean values and standard errors at each DOC concentration. The slopes and intercepts for each experiment, along with the calculated partition coefficients, are given in Table II. A general linear model was constructed to an a posteriori test for common slopes between the different DOC fractions. Significant differences (α = 0.05) between slopes were observed for humic acid and WSOC-R1, likewise for the slopes of WSOC-R1 and the other WSOC fractions. There were no significant differences between the slopes of WSOC-R1 and fulvic acid and between WSOC-R2, WSOC-R3, and WSOC-R4.

Hydrophobic organic contaminants generally exhibit less sorption to soil solution DOM or WSOC than to solutions of base-extracted soil humics, with the disparity between the NOC sorption to soil solution WSOC and base-extracted humics being dependent on the polarity of the NOC and the method of WSOC extraction. $^cK_{oc}$ values

Table III. Literature Values for Pyrene–Organic Carbon Sorption Coefficients

method	sample	$^cK_{oc}$, L kg^{-1}	ref
fluorescence quenching	humic acid	1.7×10^5	4
	fulvic acid	1.2×10^5	
	fulvic acid	5.5×10^4	
	fulvic acid	1.0×10^5	
solvent extraction	bog DOC	3.2×10^4	32
fluorescence quenching	humic acid	1.25×10^5	4
	humic acid	8.8×10^4	
	humic acid	1.61×10^5	
	humic acid	3.20×10^5	
	humic acid	2.40×10^5	
	fulvic acid	6.6×10^4	
	fulvic acid	5.4×10^4	
	fulvic acid	1.04×10^5	
	14 soils/sediments	6.27×10^4 [a]	31

[a] Average $^cK_{oc}$ value.

for pyrene sorption to humic acid, 1.7×10^5 L kg^{-1}, and to fulvic acid, 1.1×10^4 L kg^{-1}, were similar to other reported $^cK_{oc}$ values for these humics (Table III), while $^cK_{oc}$ values for pyrene sorption to most fractions of WSOC were more than 1 order of magnitude smaller. Backhus and Gschwend (*10*) have previously shown that $^cK_{oc}$ values for PAH sorption to groundwater DOM are lower than $^cK_{oc}$ values observed for base-extracted humics. The authors measured a $^cK_{oc}$ value of 2.4×10^6 L kg^{-1} for perylene sorption to Aldrich humic acid, while the $^cK_{oc}$ value for perylene sorption to groundwater DOM was less than 6.7×10^5 L kg^{-1}. For the more polar NOC, phenanthrene, the upper bounds of $^cK_{oc}$ for the sorption of phenanthrene to groundwater DOM (4×10^4–2×10^5 L kg^{-1}) were similar to values of $^cK_{oc}$ for the sorption of phenanthrene to base-extracted humic (5.0×10^4 L kg^{-1}) and fulvic acids (7.7×10^4 L kg^{-1}) (*10, 30*). In a study of the interactions of simazine with several types of DOM, Madhun et al. (*6, 8*) observed greater simazine partitioning to humic acid than WSOC. The disparity between $^cK_{oc}$ values of NOC sorption to DOM and base-extracted humics is inversely related to NOC polarity.

The technique used to extract WSOC may affect the measured interaction between NOC and WSOC and, therefore, the comparison between WSOC and base-extracted humics. Values for the $^cK_{oc}$ describing pyrene sorption to base-extracted humics were 1 order of magnitude higher than those observed for pyrene sorption to unfractionated WSOC (Table II). Observed $^cK_{oc}$ values of naphthalene sorption to WSOC, where WSOC was extracted with sonification after the soil was saturated with NaCl, were similar to $^cK_{oc}$ values for the sorption of naphthalene by humic acid (*9*). Traina et al. (*9*) found the $^cK_{oc}$ of naphthalene–WSOC to be 7.4×10^4 L kg^{-1}, while Morra et al. (*29*) found the $^cK_{oc}$ of naphthalene–humic acid to be 2.8×10^4 L kg^{-1}. The method used by Traina et al. (*9*) to extract WSOC probably extracts large amounts of humics, as evident by the dark color of the extracts reported by the authors, resulting in similar $^cK_{oc}$ values for naphthalene–WSOC and naphthalene–humic acid.

Correlation between the concentration of hydrophobic material in DOM and observed $^cK_{oc}$ is consistent with the importance of the hydrophobic component in DOM in sorbing NOC (*25*). Kukkonen et al. (*25*) fractionated aquatic DOM into hydrophobic and hydrophilic components by XAD-8 chromatography and measured naphthalene, benzo[*a*]pyrene (B*a*P), and 2,2′,5,5′-tetrachlorobiphenyl (TCB) sorption to the DOM fractions. Higher partition coefficients were observed for B*a*P and TCB sorption to the hydrophobic fractions than to the hydrophilic fractions. On the other hand, there was little difference between partition coefficients observed for naphthalene. Analysis of the hydrophobic content of DOM can give valuable qualitative information on the ability of DOM to influence NOC fate and transport in the environment. Fractionation by reversed-phase C-18 resin may provide a rapid technique to evaluate the potential for DOM to sorb NOC under different conditions.

The ability of DOM to facilitate the transport of NOC in soils is dependent on the relative sorption of NOC to DOM and the soil, the concentration of DOM in the soil solution, and the mobility of DOM (*2*). Except for the observed $^cK_{oc}$ value for pyrene sorption to WSOC-R1, $^cK_{oc}$ values for pyrene sorption to WSOC are on the order of 10^{-3} L kg^{-1} (Table II). $^cK_{oc}$ values for pyrene sorption to soils and sediments (Table III) are 1 order of magnitude higher (*31*). This indicates that the use of similar $^cK_{oc}$ values to describe NOC sorption to DOM and the solid phase may not be warranted. In addition, it shows that WSOC may not be able to compete with soil organic matter for the sorption of pyrene, and hence the facilitated transport of pyrene by WSOC may be limited. On the other hand, $^cK_{oc}$ values for pyrene sorption to WSOC-R1 and soils are of the same magnitude. Depending on the concentration of these organic colloids in soil solution and their mobility, they may have a significant impact on pyrene transport in soils.

Conclusions

Size fractions of WSOC were characterized in terms of their acidity, relative hydrophobicity, and ability to bind a nonionic organic contaminant, pyrene. Similarly characterized base-extracted humic and fulvic acids were used in this study as comparisons. Except for the largest WSOC fraction (WSOC-R1), WSOC sorbed less pyrene than humic or fulvic acid. Pyrene $^cK_{oc}$ values for WSOC ranged from 4.1×10^3 to 6.8×10^3 L kg^{-1}, while pyrene $^cK_{oc}$ values for WSOC-R1, humic acid, and fulvic acid were 1.54×10^4, 1.7×10^5, and 1.1×10^4 L kg^{-1}, respectively (Table II). Fluorescence-quenching experiments and the linear Stern–Volmer equation were used to derive these $^cK_{oc}$ values. These results indicate that the differences in $^cK_{oc}$ values for different types of organic carbon must be taken into account when the effect of DOM on NOC transport is estimated.

Ultrafiltration of WSOC was unable to create fractions of unique chemical characteristics, except for the material retained on the largest filter. This fraction, WSOC-R1, had a higher relative hydrophobicity and a larger $^cK_{oc}$ than the other WSOC fractions. The $^cK_{oc}$ value for pyrene sorption to this fraction is on the order of the $^cK_{oc}$ values for pyrene sorption to fulvic acid and soils and sediments. This property of the WSOC-R1 fraction indicates that it may represent an important fraction of total DOM capable of facilitating NOC transport, depending on its concentration in soil solutions and its mobility. More work is needed to characterize this material.

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