Organic Compounds in the Environment

Kerogen in Aquifer Material and Its Strong Sorption for Nonionic Organic Pollutants

Yong Ran, Baohua Xiao, Weilin Huang,* Ping'an Peng, Dehan Liu, Jiamo Fu, and Guoying Sheng

ABSTRACT

Sorption of organic pollutants by subsurface materials has been found to not only correlate with the total organic carbon (TOC) content, but also depend on the types of soil and sediment organic matter (SOM). Characterization of geochemically heterogeneous SOM is key to elucidating sorption mechanisms and predicting pollutant transport in ground water systems. In this study, kerogen, a nonextractable organic material, was isolated with an acid demineralization procedure from a sandy aquifer material (Borden, Ontario, Canada) having a TOC content of approximately 0.021% (w/w). Petrographical examinations reveal that the kerogen has three major types of macerals including bituminite (Kerogen Type I and II), vitrinite (Type III), and fusinite (Type IV or charred kerogen). The solid-state ^{13}C nuclear magnetic resonance (NMR) spectrum shows two dominant peaks, aliphatic and aromatic carbons, for the isolated material. Sorption isotherms measured using phenanthrene, naphthalene, 1,3,5-trichlorobenzene (TCB), and 1,2-dichlorobenzene (DCB) as sorbates showed that both the isolated kerogen and the original sand exhibited nonlinear sorption and that the phenanthrene and TCB isotherms measured for the kerogen material are more nonlinear than the respective isotherms for the original sand. The single-point organic carbon–normalized sorption capacity measured for the isolated kerogen can be several times greater than that measured for the original sand for a given sorbate. The study suggests that kerogen plays a major role in overall sorption isotherm nonlinearity and could yield higher-than-predicted sorption capacities for the subsurface material even though the content of this organic material is very low.

Sorption by soils and sediments is a major physicochemical process controlling the fate and transport of less polar organic pollutants in the subsurface. Numerous studies have shown that the equilibria and rates of sorption and desorption depend on the physicochemical properties of given organic pollutants and soils or sediments of interest (Chiou et al., 1979; Huang and Weber, 1997). For moderately hydrophobic organic contaminants (HOCs) such as phenanthrene, sorption isotherms are generally nonlinear and desorption is often hysteretic (Huang et al., 1997, 1998, 2003). Under nonequilibrium conditions, the rates of sorption and desorption are variously slow (Ball and Roberts, 1991b; Huang and Weber, 1998). Both isotherm nonlinearity and slow rate phenomena were shown to result in excessive tailing of contaminant plumes under laboratory conditions (Weber et al., 1991; National Research Council, 1994) and may be a dominant factor causing the ineffectiveness of engineered schemes for remedy of contaminated sites (National Research Council, 1994). Mechanistic understanding of the slow and nonlinear sorption and desorption processes is very important to design and implement effective technologies for remediating sites contaminated by hazardous organic contaminants.

Hydrophobic organic contaminant sorption is dominated by hydrophobic interactions with SOM (Chiou et al., 1979). Different types of SOM having different properties exhibit different sorption phenomena at both equilibrium and rate-limiting conditions. Amorphous or "soft" carbon SOM exhibits linear sorption isotherms whereas condensed or "hard" carbon SOM exhibits nonlinear and hysteretic sorption–desorption behavior (Weber et al., 1992; LeBoeuf and Weber, 1997; Huang and Weber, 1997). Humic acids in their rubbery state are examples of the soft carbon SOM and humic acids in their glassy state and coal and charcoal particles are typical hard carbon SOM (LeBoeuf and Weber, 1997; Xing and Pignatello, 1997; Song et al., 2002; Huang et al., 2003). When a soil or sediment has a low TOC content, mineral surfaces are assumed to play a significant role in the sorptive interactions, even for less hydrophobic organic contaminants such as organic solvents that have log octanol–water partition coefficients (K_{ow}) of <3 (Karickhoff, 1984). However, more and more data show that, while it is true for highly hydrophobic organic contaminants such as pyrene (Backhus and Gschwend, 1990; Schlautman and Morgan, 1994; Mader et al., 1997), nonswelling mineral surfaces have very low sorptive affinities for moderately hydrophobic organic contaminants such as phenanthrene (log $K_{ow} = 4.57$) (Mader et al., 1997; Huang et al., 1996; Piatt et al., 1996). Because the rate-limiting sorptive processes associated with mineral surfaces vs. SOM can be fundamentally and phenomenologically different (Xing and Pignatello, 1997; Huang et al., 1996; Weber and Huang, 1996), differentiating their roles in sorption is especially important for predicting fate and transport of HOCs in aquifers that are often comprised of very low TOC sandy materials.

This study examines the role of a small mass fraction of kerogen in the sorption of HOCs by an aquifer material [TOC = 0.021% (w/w)] collected from Borden, Ontario, Canada, a site that has been well characterized and used for in situ demonstration of several remediation technologies and for field-scale tracer and contaminant

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Abbreviations: DCB, 1,2-dichlorobenzene; HOC, hydrophobic organic contaminant; NMR, nuclear magnetic resonance; SOM, soil and sediment organic matter, TCB, 1,3,5-trichlorobenzene; TOC, total organic carbon; SSA, specific surface area.

transport tests (Curtis et al., 1986b; Roberts et al., 1986). The aquifer material was previously studied extensively (Ball et al., 1990) and used as a sorbent in several HOC sorption equilibrium and rate studies (e.g., Curtis et al., 1986a; Ball and Roberts, 1991a,b). These sorption studies showed that the rates of HOC uptake by the material were very slow and that the measured sorption distribution coefficients (K_d) and the ratios of the sorbent-phase concentration (q_e) to the aqueous-phase concentration (C_e) of several HOC solutes were greater than their respective K_d values predicted from hydrophobicity (i.e., K_{ow}) of the HOCs and the organic carbon fraction (f_{oc}) based on empirical log organic carbon–normalized sorption coefficient (log K_{oc})–log K_{ow} correlations. The observed overall slow rates of sorption were attributed to retarded intraparticle diffusion (Ball and Roberts, 1991b) and the higher-than-predicted sorption coefficients were attributed to binding of HOC solutes to internal mineral surfaces (Curtis et al., 1986a) or unknown high-affinity SOM (Ball, 1990).

In this study we tested the hypothesis that the Borden aquifer material contains diagenetically altered and physically condensed kerogen, which is an organic material not extractable in bases, acids, or mild organic solvents such as toluene. Prior studies showed that diagenetically altered kerogen or kerogen-containing geosorbents have K_{oc} values approximately one to two orders of magnitude higher than humic materials (Grathwohl, 1990; Weber et al., 1992; Young and Weber, 1995; Huang and Weber, 1997; Binger et al., 1999; Kleineidam et al., 1999). In this study we isolated and identified kerogen in the Borden sand. Equilibrium sorption of four different HOC solutes was measured for both the isolated SOM and the original sand. The results revealed that kerogen plays a dominant role in overall sorption by the low-TOC aquifer material.

MATERIALS AND METHODS

Sorbents and Their Characteristics

According to Ball et al. (1990), the aquifer material consists mainly of mineral grains and rock fragments of sizes ranging from approximately 850 to 75 μm. Carbonate rock fragments of biological origins (i.e., biomicrite and biosparite) are about 13 to 17% (w/w) of the bulk material. In this study, we analyzed the TOC content following the procedure described by Ball et al. (1990) and measured the N_2–Brunauer–Emmett–Teller (BET) specific surface area (SSA) and microporosity using standard techniques and 90-point N_2 adsorption–desorption isotherm data collected at liquid nitrogen temperature (ASAP-

1000; Micromeritics, Norcross, GA). Our results showed that the sandy aquifer material has low TOC [approximately 0.021% (w/w)], low SSA (approximately 0.4 m²/g), and low pore volume (<0.009 cm³/g), which are consistent with Ball et al. (1990) and Ball and Roberts (1991a).

Soil and sediment organic matter was isolated using a sequential decarbonation–demineralization procedure partly because the organic carbon is mainly associated with carbonate fragments of the sand (Ball and Roberts, 1991a). In brief, sandy material (10 kg) was weighed and placed in a series of glass flasks. Hydrochloric acid (2 M) was added at a solution to solid ratio of 4 (L) to 1 (kg) to each flask to dissolve carbonate rock fragments. After completion of decarbonation, fine particles of the treated material were transferred to Teflon bottles and rinsed three times with Milli-Q water (Millipore, Bedford, MA). Centrifugation at 6000 rpm was used for separating particles from supernatant. After rinsing, HCl (6 M) and HF [8% (w/w)] acid mixture was added to the bottles at a solution to solid ratio of about 50 (mL) to 1 (g) to dissolve silicates at a constant temperature of approximately 60°C for 48 h. Over the 48-h period, the supernatant was replaced twice with fresh HF–HCl acid mixture. After acid digestion, the solid residual was washed three times with dilute HCl and then rinsed five to seven times with Milli-Q water until the pH of the supernatant reached 6 to 7. After removal of the supernatant, the solid was oven-dried at 65°C and divided to two portions; one was stored in a glass bottle for use in sorption experiments and the other was further treated with hydrochloric acid to partially remove fluorides. The concentrated fraction was used for SOM characterization.

The isolated SOM was characterized using different techniques. Total organic C was analyzed using a high temperature combustion method on a Heraeus (Hanau, Germany) CHN-O elemental analyzer. Functionality of the isolated kerogen was determined using solid-state cross-polarization magic-angle-spinning nuclear magnetic resonance (CPMAS ^{13}C-NMR) on a 7.5-mm probe at 50 MHz carbon frequency. The organic facies and the shapes, sizes, and degree of maturation of the isolated and concentrated SOM were examined under optical microscopy of reflecting, transparent, and fluorescent modes following a procedure described in previous studies (Ran et al., 2002; Song et al., 2002).

Sorbates, Background Solutions, and Analytical Techniques

Phenanthrene, naphthalene, 1,3,5-trichlorobenzene (TCB), and 1,2-dichlorobenzene (DCB), obtained in spectrophotometric grades (>98%) from Aldrich Chemical Co. (St. Louis, MO), were used as the HOC probe solutes for this study. The octanol–water partition coefficient (log K_{ow}), aqueous solubility (C_s), and the K_{oc} values reported in the literature or estimated from empirical correlations are listed in Table 1.

Table 1. Major properties of the selected organic chemicals.†

Chemical	Molecular weight	Molar volume	log K_{ow}	C_s	K_{oc} estimated ‡	§	¶
	g/mol	cm³/mol		mg/L	L/g organic C		
Phenanthrene	178.2	152.3	4.57	1.12	22.9	17.4	6.03
Naphthalene	128.2	110.5	3.30	31.7	1.23	1.75	0.73
TCB#	181.5	125	4.02	5.36	6.46	5.93	2.42
DCB††	147.2	113	3.38	92.9	1.48	0.84	0.84

† C_s, aqueous solubility; K_{oc}, organic carbon–normalized sorption coefficient; K_{ow}, octanol–water partition coefficient.
‡ From Karickhoff et al. (1979); log K_{oc} = log K_{ow} − 0.21.
§ From Means et al. (1980); log K_{oc} = −0.686 log C_s + 4.273.
¶ From Schwarzenbach and Westall (1981); log K_{oc} = 0.72 log K_{ow} + 0.49.
# 1,3,5-Trichlorobenzene.
†† 1,2-Dichlorobenzene.

Primary stock solutions, stock solutions, background electrolyte solutions, and initial aqueous solutions were prepared following the procedure of Weber and Huang (1996). The major mineral constituent of the background solution was $CaCl_2$ at a level of 0.005 M, and 100 mg/L of NaN_3 was added to inhibit biological activity. To adjust the solution pH to 7 to 8, $NaHCO_3$ (5 mg/L) was added. Solute concentrations of the initial and equilibrated aqueous solutions were analyzed with reverse-phase high performance liquid chromatography (HPLC) (Model 1100; ODS, 5 μm, 2.1 × 250 mm C-18 column; Hewlett-Packard, Palo Alto, CA) with both diode array UV and fluorescence detection following procedures described in Ran et al. (2002) for the four HOC solutes.

Sorption Experiments

Sorption equilibria were measured using flame-sealed glass ampoules as batch systems and exactly following a procedure described in prior studies (Huang and Weber, 1997; Ran et al., 2002). The time period for measuring sorption equilibria is 42 d; our preliminary tests over 12 mo for sorption showed that this time period is sufficient for attainment of apparent sorption equilibria. Control experiments were conducted using reactors containing no sorbent for assessing loss of solutes to reactor components during sorption tests. Results showed that average system losses are consistently less than 4% of initial concentrations for the four HOCs, which is within the two standard deviations of the analyses given by the HPLC method. Hence, no correction was made during reduction of sorption data. Possible biodegradation of the solutes in the reactor systems were also checked by conducting four separate preliminary tests using a standard plating procedure as described in Huang and Weber (1998). No microorganism capable of degrading the target solutes was detected in the completely mixed batch reactors (CMBRs).

The solid-phase solute concentrations were computed based on a mass balance of solute between the solid and aqueous phases. The loss of the solutes to headspace was calculated from Henry's law constants and was considered in the mass balance calculation if it was greater than 0.2% of the total solute mass.

RESULTS AND DISCUSSION
Organic Matter Characterization

The isolated material is a gray-colored powder, contains only approximately 0.74% (w/w) of organic carbon, and has an N_2–gas SSA of 6.2 m^2/g. X-ray diffraction and petrographical examinations showed that fluorite formed during HF–HCl treatment is the dominant component of the isolated material. The fraction concentrated for both ^{13}C NMR and petrographical studies has a TOC content of 5.56% (w/w) and N and H contents of 0.34 and 1.30% (w/w), respectively. A mass-balance calculation showed that the total organic matter recovered from this procedure is approximately 18.7% of the TOC of the original sandy material. The majority of the TOC associated with the sand had not been recovered using this technique, probably due to loss of fine organic particles to decanted supernatants, or, to a lesser extent, dissolution of organic matter in aqueous solution. It may be true that a fraction of SOM associated with sand grains may not be recovered because sand grains were discarded after the first step of the isolation procedure.
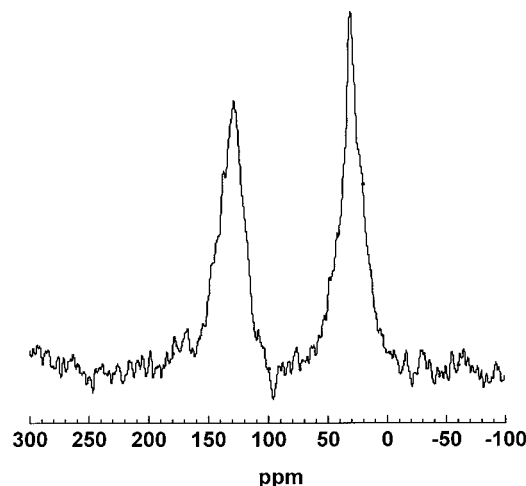

Fig. 1. Cross-polarization magic-angle-spinning nuclear magnetic resonance (CPMAS ^{13}C-NMR) spectrum for the isolated and purified soil and sediment organic matter (SOM).

The ^{13}C NMR spectrum shown in Fig. 1 has two major peaks at approximately 33 and 137 ppm, representing aliphatic (approximately 0–60 ppm) and aromatic (approximately 100–160 ppm) carbons, respectively. The integrated areas for the aliphatic and aromatic peaks are 53.4 and 46.6%, respectively. The spectrum is very similar to those we reported for the kerogen materials isolated from Altrium shales collected from Paxton Quarry of Michigan (Huang and Weber, 1997), indicating that the isolated organic matter consists mainly of kerogen.

Examinations under fluorescence microscopy (blue light excitation) and optical microscopy in both transmitted and reflected modes show that the isolated SOM is highly heterogeneous at the particle scale. As shown in Fig. 2, the organic particles are irregularly shaped and have sizes ranging from submicrometers to about 40 μm; the majority of the particles have sizes of approximately 1 to 5 μm. Observations made for 160 particles with microscopy showed that both vitrinite and bituminite or liptinite are the dominant types of macerals (40–45% each), and fusinite is a minor type of maceral. Vitrinite originates primarily from plant tissue materials and is the major component of Kerogen Type III. Liptinite or bituminite are commonly derived from animal tissues or lower level plants such as algae and are the major component of Kerogen Type I or II. Fusinite, also called black carbon or charcoal, is typically formed during incomplete oxidation of Kerogen Types I through III and is classified as Kerogen Type IV (Durand, 1980; Engel and Macko, 1993). As shown in Fig. 2, vitrinite found in the isolated SOM is tubular, angular, and opaque under transmitted microscopy. Under fluorescence microscopy vitrinite is commonly not fluorescent, and dark-gray and dark colored. Liptinites such as alginite, lipodetrinite, bituminite, suberinite, and sporinite are semitransparent under optical microscopy (transmitted mode) and are yellowish green to yellow and brownish colored and manifest an amorphous character under fluorescence microscopy. The reflectance (R_o) values measured for vitrinite and bituminite are about 0.66 to 0.82% (average of total 124 measurement points on six different slides)

and 0.1 to 0.23% (average of total 31 measurement points on two different slides), respectively, indicating relatively low maturation of the kerogen material. Fusinite and semifusinite are opaque under transmitted microscopy, not fluorescent under fluorescence microscopy, and have much higher reflectance under transmitted microscopy. They manifest a brittle or fragmented texture due to their rigid and partly combusted nature.

Sorption Isotherms

The sorption equilibrium data obtained for both the sandy material and the isolated SOM [TOC = 0.735% (w/w)] were fitted to the following Freundlich model:

$$q_e = K_F C_e^n \qquad [1]$$

or:

$$\log q_e = \log K_F + n \log C_e \qquad [2]$$

where q_e and C_e are equilibrium solute concentrations in the solid and aqueous phase expressed in units of µg/g and µg/L, respectively. The parameter K_F and the exponent n are the Freundlich capacity parameter $[(\mu g/g)/(\mu g/L)^n]$ and isotherm linearity factor, respectively. A linear regression procedure using SYSTAT Version 10.0 software (SPSS, 2000) was used for fitting Eq. [2] to the sorption data. Resulting log K_F and n parameter values, along with their 95% confidence levels, number of observations, and R^2 value, are given in Table 2. All sorption data are also shown in Fig. 3 and 4, along with the fitted isotherm parameters.

Other sorption equilibrium models tested for describing the data included the common linear and Langmuir isotherm models, the dual-domain polymer-based isotherm model (LeBoeuf and Weber, 1997; Xing and Pignatello, 1997), and the Polanyi–Manes model (Xia and Ball, 1999). The dual-domain isotherm model was found capable of describing the experimental data, but the linear and Langmuir models were not. Because they either involve more than two fitting parameters or demonstrate inadequacy for data fitting, the results of such exercises are not presented here.

To delineate the differences in sorptive properties among different sorbent–sorbate systems, single-point organic carbon–normalized sorption coefficients (K_{oc}, mL/g) were calculated using the TOC contents of the sorbents and the best-fitted Freundlich isotherm parameters (Table 2) for three different C_e levels representing 0.1, 5, and 75% of the aqueous solubility for each solute. The results are also listed in Table 2.

From the information presented in Fig. 3 and Table 2, the measured sorption isotherms are nonlinear and the single-point K_{oc} values are higher than those (Table 1) predicted from the widely used log K_{oc}–log K_{ow} correlations. Figures 3 and 4 show that the Freundlich sorption equation fits the isotherm data well in the tested C_e ranges. The values of the fitted Freundlich parameter n range from 0.69 to 0.88 for the tested sorbent–sorbate systems. For the isolated SOM, the isotherm nonlinearity appears to increase with sorbate hydrophobicity. A plot of n versus log K_{ow} yields an inverse linear relation-
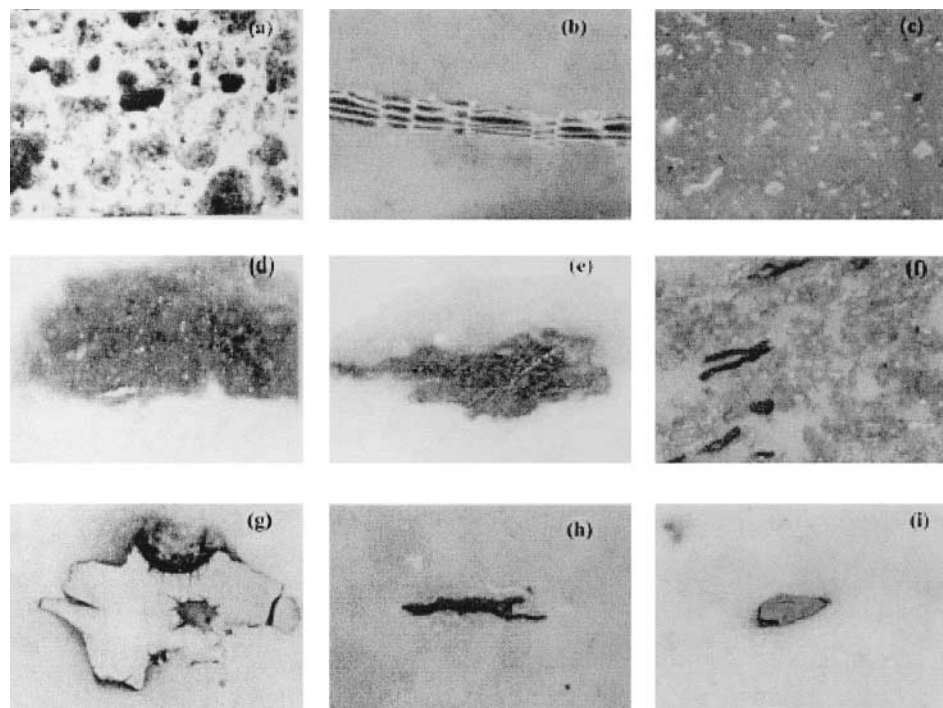

Fig. 2. Photographic illustration of the isolated and purified soil and sediment organic matter (SOM). (*a*) Organic (opaque) and inorganic (transparent) matter observed under microscope (transmitted mode) (width of photo = 101 mm). (*b*) Tubular kerogen particle consisting of cell wall (light fluorescence) and nonfluorescent vitrinite (black) (81 mm). (*c*) Laminated algae-like organic particles having light fluorescence (81 mm). (*d*) Amorphous bituminite (81 mm). (*e*) Angular vitrinite (dark) encapsulated in amorphous bituminite matrices (51 mm). (*f*) Amorphous bituminite, liptodetrinite, and sporinite, and black tubular and angular vitrinite (black) (81 mm). (*g*) Fusinite or black carbon particle (reflect mode) (gray-dark) (51 mm). (*h*) Nonfluorescent tubular vitrinite (black) surrounded by liptodetrinite (strips) (81 mm). (*i*) Angular vitrinite having reflectance (R_o) of 0.7% (reflected mode) (81 mm).

Table 2. Freundlich model parameters and the calculated concentration-dependent organic carbon–normalized sorption coefficient (K_{oc}) values for the isolated soil and sediment organic matter (SOM) and Borden, Ontario sand.

	Freundlich model parameter†			K_{oc}‡		
	log K_F	n	R^2	$C_e/C_s = 0.001$	$C_e/C_s = 0.05$	$C_e/C_s = 0.75$
	$(\mu g/g)/(\mu g/L)^n$					
			Phenanthrene			
SOM sorption	0.64 ± 0.03	0.69 ± 0.02	1.00	576	174	76
Sand sorption	-1.95 ± 0.06	0.81 ± 0.03	0.99	52	25	15
			Naphthalene			
SOM sorption	-0.87 ± 0.04	0.86 ± 0.02	1.00	11.16	6.38	4.33
Sand sorption	-3.15 ± 0.13	0.86 ± 0.04	0.99	2.08	1.21	0.83
			TCB§			
SOM sorption	-0.11 ± 0.05	0.78 ± 0.02	1.00	73.28	30.87	16.97
Sand sorption	-2.56 ± 0.09	0.88 ± 0.04	1.00	10.70	6.67	4.80
			DCB¶			
SOM sorption	-0.72 ± 0.08	0.83 ± 0.02	1.00	11.98	6.16	3.89
Sand sorption	-2.85 ± 0.25	0.84 ± 0.07	0.98	3.30	1.77	1.15

† K_F, Freundlich capacity parameter; n, isotherm linearity factor; both include 95% confidence intervals.
‡ C_e, aqueous phase concentration; C_s, aqueous solubility.
§ 1,3,5-Trichlorobenzene.
¶ 1,2-Dichlorobenzene.

ship (Fig. 5). For the original sandy material, the measured sorption isotherms are also nonlinear, but the correlation between n and log K_{ow} values may not exist among the four solutes.

The data listed in Table 2 indicate that (i) the K_{oc} values for both the original aquifer material and the SOM fraction are greater than their respective values (Table 1) predicted from log K_{oc}–log K_{ow} correlations; (ii) for a specific solute and at fixed C_e, the isolated SOM fraction has a greater K_{oc} value than the original sand; (iii) the K_{oc} value for a given solute decreases as the aqueous concentration increases; and, (iv) the K_{oc} value at a fixed C_e/C_s relative concentration increases as the hydrophobicity (i.e., K_{ow}) of the solutes increases. The K_{oc} values reported in this study for the isolated SOM can be 100 times greater than their respective
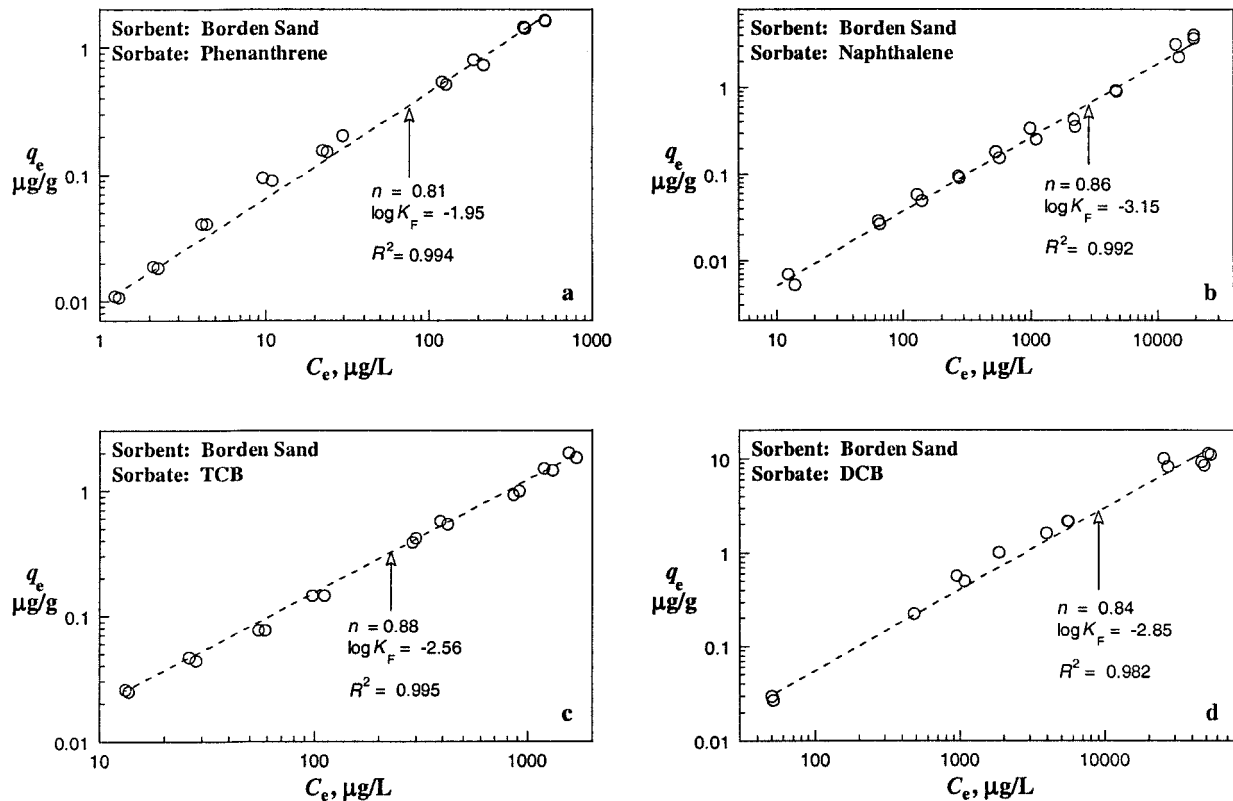

Fig. 3. Sorption isotherms measured for Borden, Ontario sand: (*a*) phenanthrene, (*b*) naphthalene, (*c*) 1,3,5-trichlorobenzene (TCB), and (*d*) 1,2-dichlorobenzene (DCB). Symbols and dashed lines represent data points and the best fit of each sorbent–sorbate data set to the Freundlich equation, respectively. C_e, aqueous-phase concentration; K_F, Freundlich capacity parameter; n, isotherm linearity factor; q_e, sorbent-phase concentration.
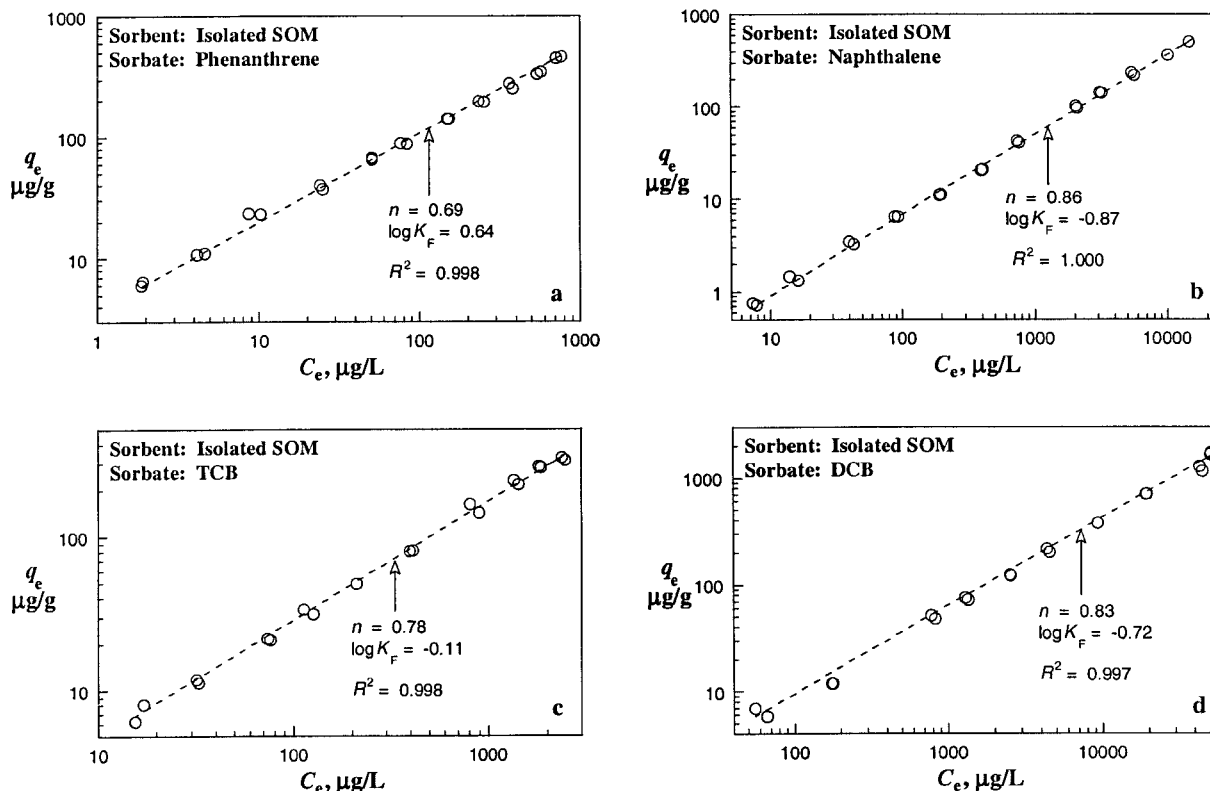
Fig. 4. Sorption isotherms measured for the isolated soil and sediment organic matter (SOM): (*a*) phenanthrene, (*b*) naphthalene, (*c*) 1,3,5-trichlorobenzene (TCB), and (*d*) 1,2-dichlorobenzene (DCB). Symbols and dashed lines represent data points and the best fit of each sorbent–sorbate data set to the Freundlich sorption equation. C_e, aqueous-phase concentration; K_F, Freundlich capacity parameter; n, isotherm linearity factor; q_e, sorbent-phase concentration.

values predicted from the widely used $\log K_{oc}$–$\log K_{ow}$ correlations such as those reported by Karickhoff et al. (1979), Means et al. (1980), and Schwarzenbach and Westall (1981). The higher-than-predicted K_{oc} values were explained in the literature via heterogeneity of SOM and nonequilibrium sorption data with C_e near C_s used for developing the linear partitioning assumption-based correlations (Weber et al., 1992; Huang et al., 1996; Xing and Pignatello, 1997; Accardi-Dey and Gschwend, 2002). Linear regressions of the $\log K_{oc}$ values calculated at three different C_e levels against the $\log K_{ow}$ values of the four HOC solutes yield the follow-

ing three empirical correlations for the isolated kerogen material (Fig. 5):

$$\log K_{oc} = 1.348 \log K_{ow} - 0.459; \; C_e \; \text{at} \; 0.001 C_s;$$
$$R^2 = 0.991 \tag{3}$$

$$\log K_{oc} = 1.151 \log K_{ow} - 0.065; \; C_e \; \text{at} \; 0.05 C_s;$$
$$R^2 = 0.991 \tag{4}$$

$$\log K_{oc} = 1.008 \log K_{ow} + 0.239; \; C_e \; \text{at} \; 0.75 C_s;$$
$$R^2 = 0.988 \tag{5}$$
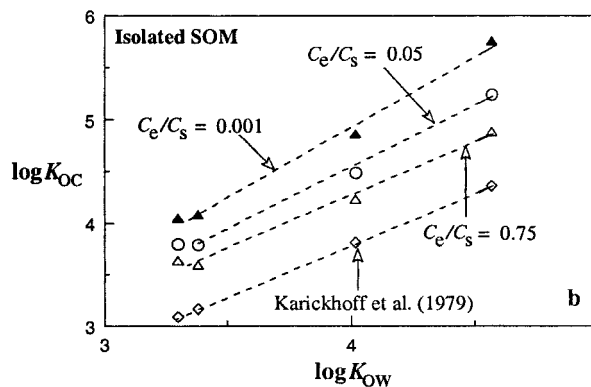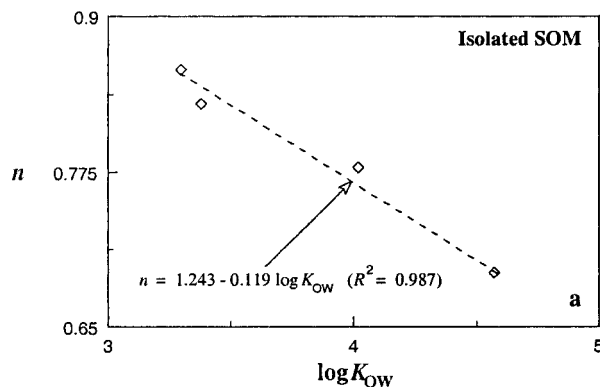
and the original aquifer material:

Fig. 5. Effects of hydrophobicity of the tested organic solutes on their (*a*) isotherm linearity (*n*) and (*b*) single-point organic carbon–normalized sorption capacities (K_{oc}) measured for the isolated soil and sediment organic matter (SOM). C_e, aqueous-phase concentration; C_s, aqueous solubility; K_{ow}, octanol–water partition coefficient.

$$\log K_{oc} = 1.039 \log K_{ow} - 0.072; \; C_e \text{ at } 0.001 C_s;$$
$$R^2 = 0.987 \tag{6}$$

$$\log K_{oc} = 1.001 \log K_{ow} - 0.183; \; C_e \text{ at } 0.05 C_s;$$
$$R^2 = 0.996 \tag{7}$$

$$\log K_{oc} = 0.974 \log K_{ow} - 0.257; \; C_e \text{ at } 0.75 C_s;$$
$$R^2 = 0.997 \tag{8}$$

The nonlinear sorption isotherms and high sorption capacities observed in this study for the original sand are consistent with prior sorption studies of three different research groups using the same aquifer material. Curtis et al. (1986a) reported higher-than-predicted K_{oc} values for five different chlorinated HOCs. Ball and Roberts (1991a) reported nonlinear sorption isotherms ($n = $ approximately 0.80) and higher-than-predicted K_{oc} values for both tetrachlorobenzene and perchloroethylene (PCE). Allen-King and Mackay (2000) found similar results for PCE. Curtis et al. (1986a) and Ball and Roberts (1991a) attributed the higher-than-predicted K_{oc} values to the HOC sorption by mineral surfaces and/ or unknown organic matter, whereas Allen-King and Mackay (2000) explained their results using the dual-mode sorption mechanisms. Alternatively, Ball (1990) and Young and Ball (1994, 1999) suggested that the Borden material may contain organic matter exhibiting high HOC sorption affinities.

The phenanthrene K_{oc} values listed in Table 2 for the isolated SOM are approximately 5 to 10 times lower than those measured for the kerogen isolated from shale in the low C_e range and approximately 2 to 4 times lower in the high C_e range (Huang and Weber, 1997). Such a difference may be related to oxidative weathering of kerogen in Borden sand. The kerogen used in a prior study (Huang and Weber, 1997, 1998) was isolated from an unweathered shale and its reducing properties may not have been altered. The kerogen found in unconsolidated sediments such as in Borden sand may have undergone various oxidative alterations during transport and deposition and its matrix may have become relatively less hydrophobic, resulting in lower K_{oc} values (Binger et al., 1999).

Roles of Kerogen versus Mineral Surfaces

The isotherm nonlinearity and higher-than-predicted K_{oc} values observed for the original sand are generally consistent with those observed for the isolated kerogen, indicating that the kerogen may have strong effects on the sorption of the HOCs by the Borden aquifer material. The fitted n values of both sorbents are nearly identical for naphthalene ($n = $ approximately 0.86) and DCB ($n = $ approximately 0.83) isotherms, whereas the n value of the original sand is 0.1 unit greater than that of the SOM isolate for phenanthrene and TCB sorption isotherms, respectively. While both the original sand and the isolated SOM exhibit higher-than-predicted K_{oc} values, the magnitudes of K_{oc} at a given C_e of a specific HOC solute differ significantly between the two sorbents. It is clear from Table 2 that the K_{oc} value of the isolated SOM can be approximately 2 to 10 times greater than that of the original sand at a given C_e/C_s level of a specific HOC solute tested.

To quantitatively illustrate the role of kerogen in the sorption of the bulk sand, a mass balance calculation was performed based on sorption isotherm parameters, the mass of kerogen recovered, and the TOC of the kerogen and the original sand. The results indicate that the kerogen may account for about 63 to 68% of DCB sorption capacity of the original sand and that sorption to kerogen could exceed the actual sorption capacity of the original sand for the other three sorbates at low solute concentrations. For instance, phenanthrene sorption capacity of kerogen on a 18.7% (w/w) basis is twice that of original sand at $C_e/C_s = 0.001$.

The calculated higher-than-actual sorption capacity and the fact that the isolated kerogen only constituted 18.7% of the TOC of the original sand suggest that the sorption property of the kerogen associated with the original sand may differ from that of the isolated kerogen. One explanation may be the inaccessibility of the sorption "sites" of kerogen associated with original sand to HOC solutes. Because the majority of SOM in Borden material is associated with the carbonate fragments (Ball et al., 1990), it is reasonable to assume that a fraction of the carbonate-encapsulated kerogen would be inaccessible to HOC molecules during sorption even over a time period of six weeks. To test this hypothesis, we conducted a separate batch sorption experiment by completely decarbonating Borden material and hence exposing SOM to the solution phase before the sorption test. The decarbonation was done in individual batch reactors using dilute HCl acid. After rinsing the treated sandy material with Milli-Q water, each reactor was filled with initial aqueous phenanthrene solution and allowed to attain apparent sorption equilibrium. The measured sorption isotherm is shown in Fig. 6a, along with the isotherm measured simultaneously for the original sand. It is clear from the figure that there is no measurable difference between the original and HCl-treated sand, consistent with the observation of Ball and Roberts (1991a) for tetrachlorobenzene. This suggests that the observed discrepancy is probably not related to solute inaccessibility to SOM entrapped in the carbonates.

An alternative explanation is that the kerogen isolated from the sand may have been modified by a more severe HF–HCl treatment and hence be cleaner than when it is associated with the original sand. The HF–HCl may react with kerogen, loosen its matrix, and increase its porosity, enhancing sorption capacity for HOCs. Coatings of inorganic materials such as silicates and aluminum silicates on external and internal surfaces of kerogen particles can lower the accessibility of its sorption "sites" to HOC sorbate molecules. Unlike carbonate coatings, silicate coatings cannot be removed in HCl solution, but can be removed by the HF–HCl treatment, yielding increased HOC sorption capacity for the kerogen.

To estimate the contribution of the unaltered kerogen to the sorption by the overall original sand, we conducted a separate phenanthrene sorption experiment using the sand after nondestructive removal of light OC particles
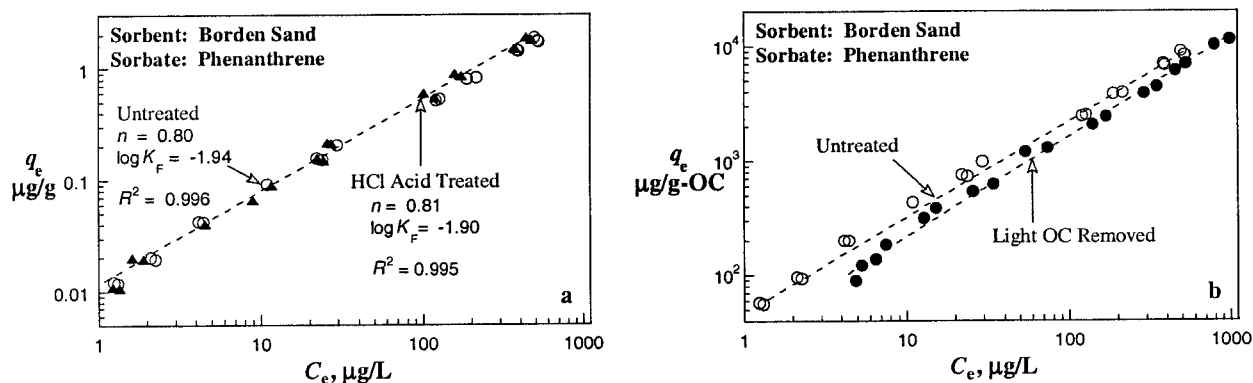
Fig. 6. Phenanthrene sorption isotherms measured for the (*a*) original, HCl⁻ and (*b*) light organic carbon (OC)–free materials from Borden, Ontario. C_e, aqueous-phase concentration; K_F, Freundlich capacity parameter; n, isotherm linearity factor; q_e, sorbent-phase concentration.

with a dense aqueous $ZnBr_2$ solution. The separation of light OC was performed in a beaker at a solution to sand ratio of 5 (mL) to 1 (g). The $ZnBr_2$ solution allowed low-density organic particles (<2.0 g/mL) to separate from the bulk sand by gravity (Karapanagioti et al., 2001). Total organic C analysis showed that the separation procedure reduced TOC of the sand by 10 to 12%. Under the microscope, the organic matter removed by gravity separation exhibits similar properties as those isolated by acid treatment (Fig. 2). Its relatively large size (approximately 10–100 μm) and low density suggest that the particulate material is probably not present in carbonate rock fragments. It may be present in the sand as discrete particles. The best fitted n and log K_F values of the phenanthrene sorption isotherm measured for the light OC-free sand are 0.87 and −2.25, respectively, compared with 0.80 and −1.94, respectively, for the original sand. The measured phenanthrene sorption isotherm, along with that of the original sand, is presented in Fig. 6b, in which the q_e data are normalized to organic carbon mass for better comparison of sorption capacity in the presence and absence of the light OC fraction. It is clear from the figure that the sand free of light OC has significantly lower organic carbon–normalized sorption capacity and a more linear isotherm than the untreated sand. The differences in the single-point K_{oc} values calculated from the best-fit isotherm parameters are 16% (C_e = 600 μg/L) to 60% (C_e = 6 μg/L) between the light OC-free and untreated sand, suggesting that the majority of the organic matter associated with the sand has lower sorption capacity than the discrete lighter OC fraction. If the lighter OC is the same organic material isolated in the acid digestion procedure, the kerogen that constituted 18.7% of the TOC of the original sand could account for 36 to 69% of the phenanthrene sorption capacity for the sand.

The role of mineral surfaces in the overall sorption is probably insignificant, as demonstrated in the following calculation. Using the mass-based phenanthrene K_d value of 1.2×10^{-3} L/g reported by Huang et al. (1996) for a natural quartz sample (N_2–BET SSA = 6.53 m²/g) and assuming that sorption on mineral surfaces follows a partitioning mechanism within the immobile surface water layer (Huang et al., 1996), the K_d value for sorp-

tion of phenanthrene on the inorganic surfaces of the isolated SOM is approximately 1.2×10^{-3} L/g for an SSA of 6.2 m²/g. This estimated K_d value is much smaller than the lowest phenanthrene K_d value (0.6 L/g) measured for the isolated SOM. A similar calculation can demonstrate that the mineral surfaces of the Borden material having a SSA of 0.4 m²/g contribute about 1 to 2% of the overall phenanthrene K_d value ($\geq 4 \times 10^{-3}$ L/g) measured for the bulk sand.

CONCLUSIONS

This study suggests that, even when present in a very small mass fraction, kerogen can play an important role in isotherm nonlinearity and the high sorption capacity exhibited by the bulk sand. As indicated in a recent study (Song et al., 2002), particulate organic materials such as kerogen and black carbon are probably the dominant components of the operationally defined humin fractions in soils and sediments. Depending on their contents in the bulk sorbents, these materials may control the overall sorption and desorption processes for HOCs in soils and sediments (Accardi-Dey and Gschwend, 2002; Karapanagioti et al., 2001; Binger et al., 1999; Weber et al., 1992). Accurate determination and adequate characterization of SOM is thus key to prediction of fate and transport of organic pollutants in the subsurface.

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