A Distributed Reactivity Model for Sorption by Soils and Sediments. 12. Effects of Subcritical Water Extraction and Alterations of Soil Organic Matter on Sorption Equilibria

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Subcritical water extraction was used as a tool to remove the carboxylic, aliphatic, and carbohydrate types of organic carbon from a humic soil. The rates and extents of soil organic carbon removal were quantified as functions of superheated water temperature, phase, and exposure time. The experimental data suggest that superheated water effects deoxygenation/aromatization reactions of soil organic matter that mimic those of geologically slow, natural diagenesis processes. Phenanthrene sorption and desorption equilibrium isotherms for the altered soils were measured. The sorption isotherms were characterized by increasing capacity and nonlinearity with increasing degree of polar functionality removal and simulated diagenesis of the soil organic matter.

Introduction

Sorption processes play a dominant role in the transport and ultimate fate of organic contaminants in subsurface systems. Accurate mechanistic characterizations of these processes are crucial for reliable estimates of the effects of organic contaminant release and for design of appropriate remediation strategies. Soil and sediment organic matter (SOM) is generally the dominant domain for sorption of hydrophobic organic contaminants (HOCs), and the molecular characteristics of SOM have proven to affect sorption properties (*1−16*) that are manifest in isotherm nonlinearity (*6−16*) and sorption/desorption hysteresis (*14−16*). The chemical and structural properties of soil and sediment organic matter can vary widely from one sample to another at the macroscopic scale, and significant ranges of property heterogeneity can often be found at the microscopic scale as well. This is not surprising in that such materials derive from a variety of organic precursors and debris, comprising highly complex composites of partially or completely degraded biomolecules. Carbohydrates, lipids, and proteins from decaying plants, animals, and microorganisms progressively change because of early diagenesis related mainly to the activity of microorganisms living in sediments (*17−19*). This young organic matter is transformed by such activity to humic and fulvic acids, humins, and eventually by additional processes to mature, condensed, primarily aromatic kerogens over geological time (*17−19*). Conclusions relating the HOC sorption behavior of soils and sediments to their degree of natural organic matter maturation via diagenesis processes such as condensation and aromatization have been made (*4, 7, 9−10, 14−16*).

In one of the first attempts to characterize and quantify the phenomenological effects of diagenetic condensation processes on contaminant sorption, Weber et al. introduced the concept of "soft" and "hard" carbon (*9*). The terms were meant not to define two distinctly different types of carbon, but rather to introduce two operational measures that might be used to correlate organic matter maturation and heterogeneity with observed differences in soil or sediment sorption behavior. The objective of this study is to explore further the relationships between soil/sediment organic matter characteristics and the sorption/desorption behaviors of hydrophobic organic contaminants. To do this, we introduce rapid diagenesis-like changes in organic matter of a soil in subcritical water and relate these observed alterations to the subsequent equilibrium sorption/desorption properties of the soil with respect to phenanthrene, a representative target HOC.

Subcritical water has several properties that make it attractive as a solvent for extraction and reaction of organics. The term subcritical refers to water at elevated temperatures and pressures approaching but not in excess of the critical point (i.e., T_c = 374 °C and P_c = 218 atm). Because of its significantly lower dielectric constant, which drops from about 80 at room temperature down to 26.8 at 250 °C (*20*), subcritical water is capable of dissolving many organic compounds that are not soluble at ambient conditions. The density and dielectric constant of water at 300 °C approach those of ambient acetone (*21, 22*). Subcritical water has been used successfully to selectively extract different classes of organic compounds ranging from polar phenols to nonpolar polynuclear aromatic hydrocarbons and alkanes simply by changing the temperature and pressure of the water (*23−25*). High solubilities of nonpolar organics in subcritical water have been reported by others (*26, 27*). It is also well established that reactions of organic compounds take place rapidly in "neutral" subcritical water that include deoxygenation, aromatization, condensation, hydrolysis, bond cleavage, and autocatalysis reactions. This body of literature is reviewed in Siskin (*28*) and Katritzky (*29*). Siskin (*28*) proposes that many of these rapid laboratory reactions are analogous to reactions that occur over geological time in nature to form kerogen from plant and animal source material. The deoxygenation and aromatization processes that take place in subcritical water thus mimic the natural diagenesis of soil organic matter (*28*). The work described here examines subcritical water at two temperatures, 150 °C and 250 °C, and in two different phases, liquid and steam, for extracting and altering the natural organic matter of a geologically young top soil. Studies of sorption equilibria for uptake of phenanthrene by variously treated soil samples reveal information about sorption mechanisms associated with different types of soil organic matter.

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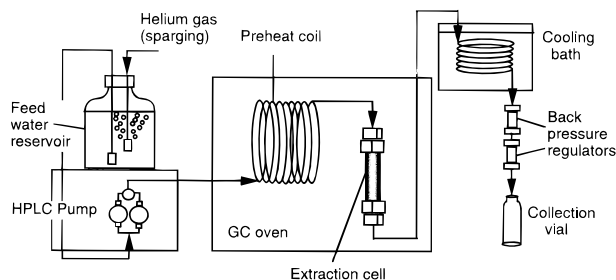‡ Drexel University.
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FIGURE 1. Schematic diagram of the subcritical water extraction (SUBWAX) system.

Experimental Section

Subcritical Water Extraction. A subcritical water extraction (SUBWAX) system modeled after one designed by Hawthorne (*25*) was fabricated for extraction of up to six grams of soil with water at elevated temperatures and pressures. A schematic diagram of the system is shown in Figure 1. Extractions were performed in a manner analogous to conventional supercritical fluid extraction. Distilled, deionized water (Nanopure, Barnsted Corp.) was helium sparged in a 2-liter HPLC solvent reservoir and pumped (Dionex model APM-2 isocratic dual piston pump) through the wall of a GC oven (Hewlett-Packard model 6890) in stainless steel tubing (1/16 in. o.d., 0.02 in. i.d.; Alltech Chromatography) wrapped in a 10-m preheat coil to an 8-ml sample cell. The sample cell was constructed from HPLC mirror-finish tubing (4 in. length of 1/2 in. o.d. by 10 mm i.d.; Alltech Chromatography), 1/2 to 1/16 in. column end fittings (Valco Instruments), bearing spacers (W. M. Berg, Inc.), and stainless steel replacement frits for 1/2 in. tubing (Parker Fluid Connectors). Water flowed from top to bottom through the vertically mounted sample cell, first through a 10-mm deep plug of stainless steel packing material (1.0-mm cut wire, Abrasive Materials, Inc., Fortville, IN) to eliminate wall effects due to laminar flow and then through the soil sample to be extracted. The 2-μm stainless steel frit supported the soil column and contained the sample in the cell. From the sample cell the water flowed out from the oven through 1/16 in. tubing into a 5-m cooling coil in a water bath maintained at ambient temperature. The cooled water then flowed through a series of back-pressure regulators (Upchurch Scientific, Inc.) to lower its pressure to atmospheric. The cooled water containing the extracted dissolved organics was sequentially collected in a series of covered 40-mL glass vials. Organic matter losses to the system in the cooling coil were determined by mass balances to be insignificant. The steam extractions differed from the liquid water extractions in that the cooling coil was shortened and no back pressure regulators were utilized. Each extraction began with a 10-min heating stage preceding initiation of flow.

The helium-sparged, distilled, deionized water was sampled into gastight Teflon-sealed crimped-top vials and measured by GC headspace analysis (GOW-MAC series 580, Lehigh Valley, PA) to verify that it did not contain dissolved oxygen. Concentrations of soil organic carbon and inorganic carbon in the collected subcritical water extracts were measured using a Shimadzu model TOC-500 total organic carbon analyzer (Shimadzu Corporation). The aqueous samples obtained from the extraction were also analyzed by GC/MS, for which a DB-5, 0.25-mm i.d., 30-m column provided adequate gas chromatographic resolution. Electron impact spectra were provided by a Finnigan Incos 50 quadrupole mass spectrometer, and chemical ionization spectra were obtained on a Varian Saturn 2000 ion trap.

Sorbents. A topsoil that contains 5.6% soil organic carbon that is primarily humic in character was collected near Chelsea, Michigan. The soil was dried, sieved to pass through a 2-mm screen, and riffle-split to obtain representative samples. Six samples of this Chelsea soil were extracted under different subcritical water conditions (Table 1) and retained for characterization and sorption/desorption investigations.

The original soil and extracted samples were characterized by N$_2$-based (99.9995%, BOC Gases) BET surface areas at 77 K using a Micromeritics accelerated surface area and Porosimitry (ASAP) model 2010. Each sample was sieved before surface area analysis so that only the 38–180 μm size fraction was measured. Elemental analyses of carbon, hydrogen, oxygen, nitrogen, and ash were determined for each sample by Huffman Laboratories, Golden, CO. Detailed experimental methods for the elemental analysis are presented in Huffman and Stuber (*30*). Solid state ^{13}C NMR measurements were made using a Chemagnetics 100/200 solids NMR spectrometer (Western Research Institute, Laramie, Wyoming). Spectra were recorded at 25 MHz using the technique of cross-polarization (CP) with magic angle spinning (MAS) and high-power decoupling. Because of the low total organic carbon (TOC) values for the soils, measurements were made using a large-volume sample spinner (2.1 mL) and a spinning rate of about 3.8 kHz. Typically, 54 000 transients were recorded because of the low TOCs. A 50 Hz exponential multiplier was applied to the free induction decay of each ^{13}C spectrum before integration.

Solute. Spectrophotometric-grade phenanthrene was obtained from Aldrich Chemical Co., Inc. Stock solutions were prepared by dissolving the phenanthrene in HPLC-grade methanol, and aqueous solutions were prepared by addition of stock solution to distilled, deionized water (Nanopure, Barnsted Corp). The aqueous solutions also contained 0.005 M CaCl$_2$ as a mineral constituent, 100 mg/L NaN$_3$ to control biological activity, and 0.005 g/L NaHCO$_3$ to buffer at pH 7.0. In all experiments, the methanol concentrations in the aqueous samples were less than 0.2 vol %.

Sorption and Desorption Experiments. Established bottle-point, fixed dosage completely mixed batch reactor (CMBR) procedures were used in all adsorption and desorption experiments. Previous studies provide experimental details (*11, 14, 16*). Flame-sealed glass ampules were used as CMBRs to minimize system losses of phenanthrene. Preliminary investigations showed that three weeks was an adequate time in which to attain apparent sorption equilibrium for all systems examined. After a three-week sorption step, the solution phase of each reactor was sampled, the solutions were separated from the soils in the ampules, and each ampule was refilled with solute-free buffer solution, resealed, and completely mixed end over end again for the subsequent three-week desorption equilibrium step.

All phenanthrene concentrations were analyzed by reverse-phase HPLC (Hewlett-Packard model 1090, ODS, 5 μm, 2.1 $\times$ 250 mm column); a diode array detector was employed for concentrations between 30 and 1000 μg/L and a fluorescence detector for concentrations between 0.5 and 30 μg/L. Solid-phase concentrations were calculated by a mass balance on each CMBR.

TABLE 1. Subcritical Water Conditions Used to Generate Pre-Extracted Soil Samples

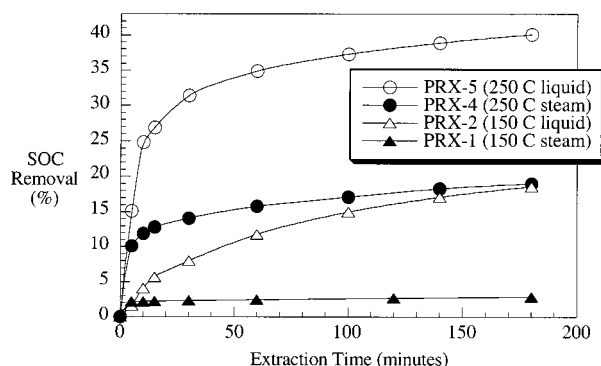| sample name	time (h)	temp (°C)	water phase	pressure (atm)	flow rate (mL/min)
PRX-1	3	150	steam	3–4	0.5
PRX-2	3	150	liquid	75–90	1
PRX-3	0.5	250	liquid	60–90	1
PRX-4	3	250	steam	12–13	1
PRX-5	3	250	liquid	70–120	1
PRX-6	10	250	liquid	80–90	1

FIGURE 2. Dynamic subcritical water extraction of soil organic carbon from Chelsea soil.

The Freundlich isotherm model was used for analysis of the equilibrium sorption and desorption data. This model has the form:

$$q_e = K_F \, C_e^{\,n} \tag{1}$$

where q_e is the solid-phase equilibrium concentration and C_e is the liquid-phase equilibrium concentration. The parameter K_F is the Freundlich unit-capacity coefficient, and n is a joint measure of both the relative magnitude and diversity of energies associated with a particular sorption process (*31*). Isotherm parameters were calculated from logarithmically transformed data using SYSTAT software (Version 5.2.1, SYSTAT, Inc.).

Results and Discussion

Subcritical Water Extraction. Preliminary studies showed that the water temperature, phase, and cumulative time of exposure to sample were dominant factors for dictating the rate and extent of soil organic matter extraction. Pressure changes did not significantly impact extraction by liquid-phase water, which is consistent with the fact that the dielectric constant of water is a strong function of temperature and phase but a weak function of pressure (*20*). Pressures above about 40 atm are required to keep 250 °C water in the liquid phase (*32*), so water pressures safely above this level were maintained in all liquid extractions.

Extraction of soil organic carbon as a function of time is plotted in Figure 2. The liquid water removes more soil organic carbon than steam at each temperature, and the higher temperature removes more soil organic carbon for each phase. The reason that liquid water removes more carbon from the soil than the steam is most likely because the humic organic matter of this geologically immature soil contains many polar functional groups that can more readily associate with water. There are probably several reasons why increasing temperature increases the removal of soil organic components. For liquid water, the dielectric constant decreases with increasing temperature, thus increasing the solubility of organics. For both the liquid water and the steam, increasing temperature provides more energy for breaking bonds and releasing organic carbon from the soil matrix. Further, the chemical alterations that are expected to take place at the higher temperatures can release organic reaction products that might not be generated at the lower temperatures.

GC/MS analyses of the soluble (or at least nonsettleable) organic fragments from the 250 °C liquid and steam extractions are shown in Figure 3. There are limitations to the conclusions that can be drawn from this analysis, namely: (i) we cannot be certain that the larger extracted organic fragments made it through the GC column; (ii) the mass spec identification was accomplished only by library match-

ing; and (iii) the large variety of molecules generated overlapping peaks. Nonetheless, these data do give a qualitative flavor for the types of extracted compounds and their dominant functional groups. Molecular structures are indicated for a few selected peaks in Figure 3. The principal organic functional groups present consisted of carboxylic C, aromatic/phenolic C, and oxygenated aliphatic C, which corresponds to the fact that the soil organic matter is known to be humic in character. We also observed some of the same organic compounds in both the liquid and the steam extracts, as seen in Figure 3(a) and (b) at 32.0 and 39.3 min.

In addition to these aqueous extract characterizations, the treated soils were analyzed by solid state ^{13}C NMR both before and after the 10-h 250 °C liquid extraction. These analyses are illustrated in Figure 4. Figure 4(a) shows the ^{13}C NMR spectrum for the original Chelsea soil prior to extraction, while Figure 4(b) shows the spectrum for a soil extracted with 250 °C liquid subcritical water for 10 h. In general, ^{13}C NMR spectra can be interpreted within the 0−220 ppm range by assigning the respective chemical shift peak areas to aliphatic C (0−50 ppm chemical shift), carbohydrate C (50−105 ppm), aromatic C (105−160 ppm), carboxylic C (160−187 ppm), and carbonyl C (187−220 ppm) (*33−36*). These reported chemical shift ranges vary by a few ppm from reference to reference, which is not surprising because there is in fact slight overlap of the crudely assigned regions. The NMR spectrum in Figure 4(a), with four dominant peaks in the aliphatic, carbohydrate, aromatic, and carboxylic carbon regions, is characteristic of spectra for most humic-type soil organic matter. Figure 4(b), the ^{13}C NMR spectrum for a subcritical water extracted Chelsea soil, reveals that the majority of the organic carbon with aliphatic, carbohydrate, and carboxylic functionality has been removed, and the remaining carbon is primarily aromatic. Approximate mass balances of the amount of soil aromatic carbon helps to explain why we conclude that aromatization reactions took place during subcritical water extraction. The peak areas in specific regions are approximate quantitative indicators of the amount of carbon atoms with the designated functionality. Integration of the total carbon spectrum in Figure 4(a) gives an aromatic carbon mass fraction in the original Chelsea soil of 23%. Similar integration of the peaks in Figure 4(b), the soil sample from which 50% of the total organic carbon was removed, yields an aromatic carbon mass fraction of about 66%. Since GC/MS analyses suggest that the carbon in the aqueous extracts is at least 20% aromatic, the total aromatic carbon in the system, extracted plus unextracted, increased by a factor of at least 1.8. This indicates that new aromatic material is being generated in the subcritical water that was not present prior to extraction.

A comparison between the specific surface area values of the original Chelsea soil and four of the extracted soil samples is given in Table 2. As the subcritical water extraction conditions become increasingly stringent, the BET−N₂ surface areas of the soil samples increase.

Sorption Experiments. Three-week phenanthrene sorption isotherms for pre-extracted soils are presented in Figures 5 and 6. Figure 5 illustrates the effects of pre-extraction time on subsequent sorption equilibria for soil samples extracted with 250 °C liquid subcritical water, and Figure 6 illustrates the effects of different pre-extraction temperatures and phase conditions. The isotherms in both figures are compared to the isotherm determined in previous studies for the natural (unextracted) Chelsea soil (*13*).

It is clear from the isotherms shown in Figure 5 that increasing the SUBWAX time significantly increased the organic carbon normalized sorption capacity over the entire concentration range investigated. Table 3(a) presents the trends in K_{oc}, the concentration-dependent carbon-normalized distribution coefficient calculated at two residual
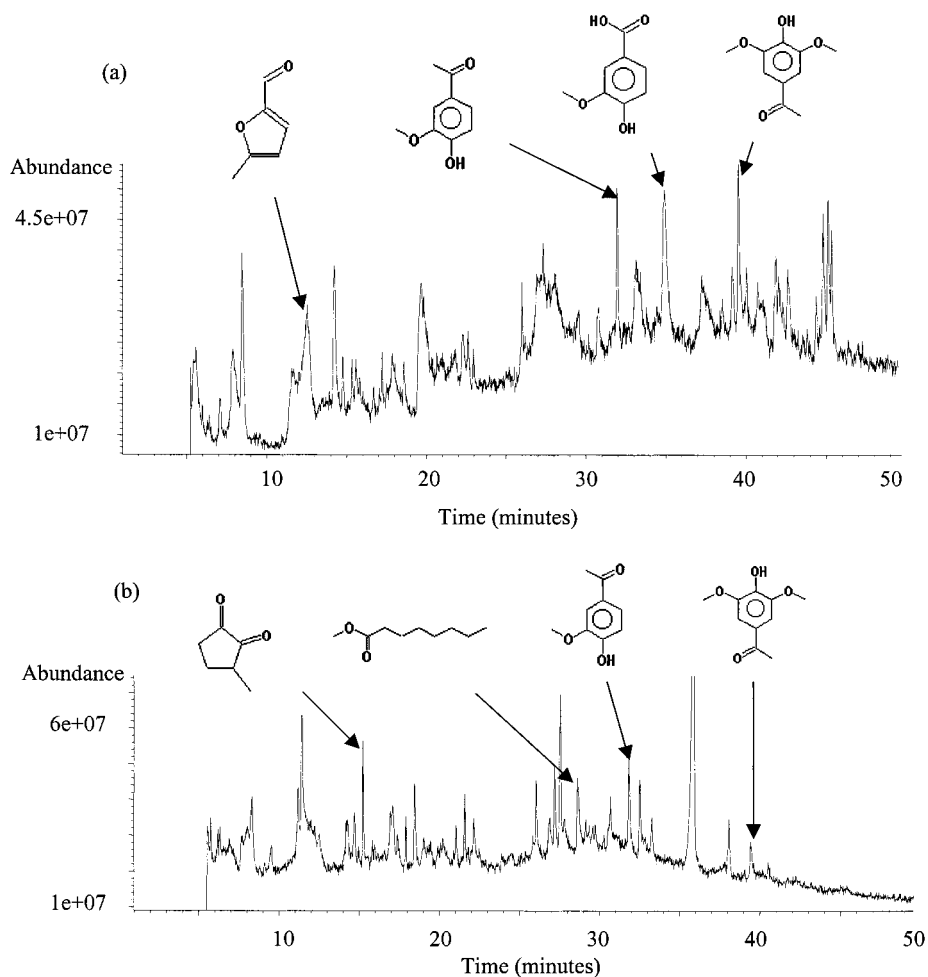
FIGURE 3. GC/MS chromatograms of aqueous extracts removed from Chelsea soil by subcritical water extraction: (a) 250 °C liquid water extract, (b) 250 °C steam extract. Selected peaks are designated by the organic molecule structures identified through GC/MS library matching.
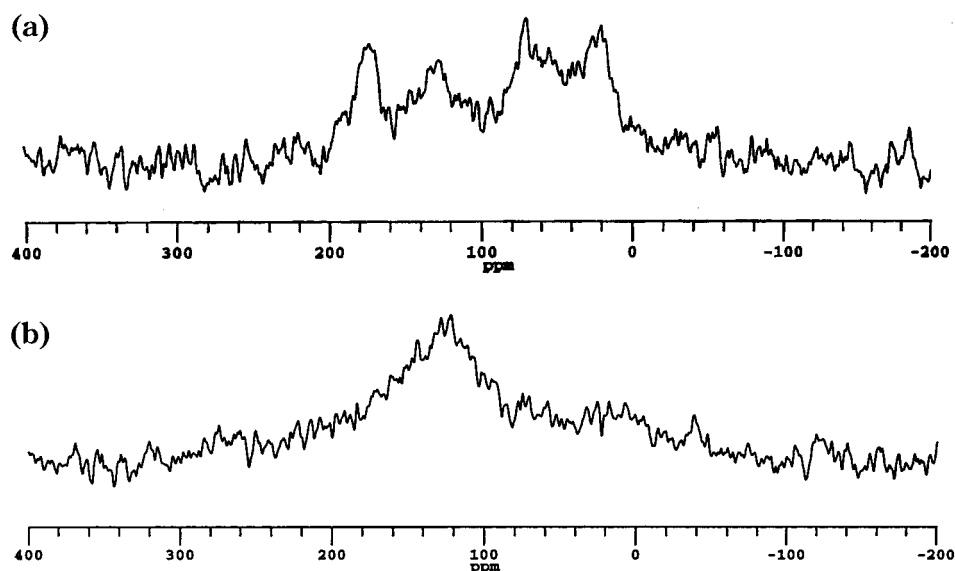

FIGURE 4. (a) ^{13}C NMR spectrum for original (unextracted) Chelsea soil. (b) ^{13}C NMR spectrum for Chelsea soil extracted with 250 °C liquid water for 10 h (PRX-6).

solution phase phenanthrene concentrations, 1 and 1000 ppb. These represent the bounds of the lowest and highest decades of measured residual concentration. Values of this coefficient increase by more than an order of magnitude at the 1 ppb aqueous phase concentration level and by a factor of 5 at the 1000 ppb level as the time of 250 °C water pre-extraction increases from 0 to 10 h (original soil, PRX-3, PRX-5, and PRX-6). The sorption isotherms also become more nonlinear for soil samples subjected to longer subcritical water extraction times, as evidenced in Table 3(a) by the

TABLE 2. Elemental Analysis of the Extracted Soil Samples

	original[a]	PRX-1	PRX-2	PRX-3	PRX-4	PRX-5	PRX-6
carbon (%)	5.62	5.59	4.72	3.74	4.43	2.99	2.67
hydrogen (%)	0.87	0.84	0.78	0.60	0.64	0.65	0.58
oxygen (%)	9.11	8.86	8.24	7.03	7.23	6.32	5.68
nitrogen (%)	0.42	0.41	0.31	0.18	0.31	0.12	0.09
ash (%)	84.73	86.51	89.00	91.75	89.78	92.75	93.96
BET−N_2 S.A.[b]	4.12	ND	4.76	ND	4.94	7.85	8.42

[a] Unextracted Chelsea soil. [b] BET-N_2 surface area in units of m2/g. (Standard deviation of specific surface area was less than 0.05 m2/g for all measurements.)
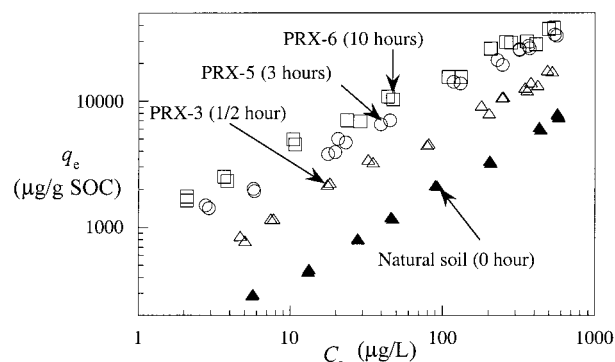

FIGURE 5. Organic carbon normalized phenanthrene sorption isotherms for original Chelsea soil and for soil samples pre-extracted by 250 °C liquid subcritical water for the time periods indicated.
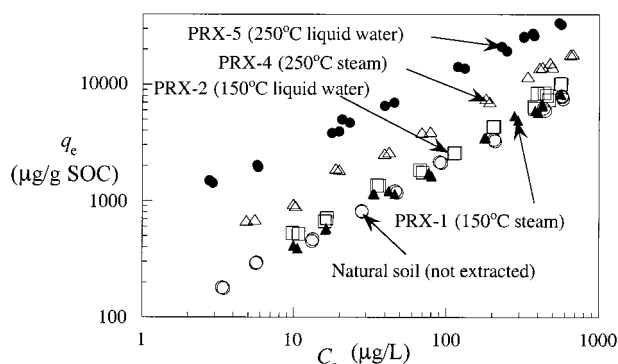

FIGURE 6. Organic carbon normalized phenanthrene sorption isotherms for original Chelsea soil and for soil samples pre-extracted for 3 h by subcritical water at different phase and temperature conditions.

decreasing trend in Freundlich *n* values from 0.722 to 0.559 for the same samples.

Figure 6 illustrates that the 250 °C steam pre-extraction also produced a soil sample (PRX-4) having an SOC-normalized sorption capacity significantly higher than that of the original soil, but the increase in nonlinearity was smaller than that which resulted from the liquid water extractions. Table 3(a) contains the corresponding phenanthrene isotherm parameters. Neither the 150 °C liquid nor the 150 °C steam pre-extraction conditions had significant effects on the organic carbon normalized parameters of subsequent phenanthrene sorption, also shown in Figure 6 and Table 3(a).

The trends evident in Figures 5 and 6 and Table 3(a) can be related to differences in the mechanisms of solute sorption by different types of natural organic material. There may be many reasons why the organic carbon normalized phenan-threne distribution coefficient increases for soils with in-creasing 250 °C liquid pre-extraction time.

First, sorption properties may change because SUBWAX increases the surface area of soil organic matter. It is expected

that the removal of humic soil organic matter opens up pores and breaks up aggregates, which, because soil organic matter is usually finely dispersed within the mineral phases (*17*), should increase the specific surface area available for adsorption onto tightly bound, condensed organic matter. The data in Table 2 verify that soil surface area increases with SUBWAX. Decreasing Freundlich *n* values with increas-ing pre-extraction time (Table 3(a)) also suggest that sorption becomes more of an *ad*sorption and less of and *ab*sorption, or partitioning, process.

Second, as the polar functional groups are removed from the soil organic matter, a more hydrophobic SOM matrix is left behind which may be more attractive for sorption of phenanthrene. The ^{13}C NMR data verifies that aromaticity increases and the oxygen functionality of soil organic matter decreases in the 250 °C subcritical water.

Third, and most important, the reactions that take place in the subcritical water to alter the organic matter remaining on the soil may create SOM matrixes having enhanced sorption characteristics. We mentioned above that deoxy-genation and aromatization reactions of organic compounds known to occur rapidly in "neutral" superheated water can mimic the natural diagenetic processes of geological time. This pseudodiagenesis may increase the capacity and non-linearity of phenanthrene sorption. In fact, the organic carbon normalized isotherm parameters determined for phenan-threne sorption by the soil sample pre-extracted at 250 °C for 10 h are comparable to those of kerogen-containing shales and coal reported previously (*10, 12, 14*).

We are compelled to believe that these pseudodiagenesis alterations are significant for several reasons. Not only does K_{OC} increase for pre-extracted soils, but the nonnormalized distribution coefficients, K_D, also increase by nearly an order of magnitude, even though up to half of the organic carbon was removed from the soil (Table 3a). Furthermore, the 10 hour pre-extraction (PRX-6) removed only 6% more soil organic carbon than the 3 h extraction at the same tem-perature and phase conditions (PRX-5), but this effected a 75% difference in K_{OC} increase at the 1 ppb phenanthrene solution level. In addition, the changes in isotherm param-eters by the 250 °C steam pre-extractions were far more significant than those yielded by the 150 °C liquid water pre-extractions, even though these two conditions removed about the same amount of soil organic carbon. This is probably because significant organic reactions did not take place at the lower temperature, which is expected on the basis of the work of Siskin and Katritzky (*28*) on deoxygenation and aromatization reactions at temperatures between 250 and 350 °C.

Desorption Experiments. Desorption equilibrium data are presented in Table 3(b). The sorption/desorption equi-librium data corresponding to the PRX-6 sample, which is representative of the isotherm data for all six extracted soil samples, are plotted in Figure 7. Sorption-desorption hys-teresis was quantified using the hysteresis index defined in our previous studies (*14, 15*):

$$H.I. = \frac{q_e^d - q_e^s}{q_e^s}\Bigg|_{T,C_e} \qquad (2)$$

where q_e^s and q_e^d are the solid-phase concentrations for sorption and desorption, respectively, and the subscripts *T* and c_e specify conditions of constant temperature and equilibrium aqueous phase concentration.

Previous studies showed that apparent sorption−desorp-tion hysteresis exhibited by younger humus-rich natural sorbents is significantly less than that exhibited by geologi-cally older kerogen materials (*14−16*). Generally, natural

TABLE 3

(a) Sorption Isotherm Parameters and Calculated Concentration-Dependent Distribution Coefficients

sorbent	sorption parameters				K_{OC} (L/g OC)[c]		K_D (L/g soil)	
	$\log K_F$[a]	n	R^2	N[b]	$C_e = 1\ \mu g/L$	$C_e = 1000\ \mu g/L$	$C_e = 1\ \mu g/L$	$C_e = 1000\ \mu g/L$
original soil	0.644 (0.022)[d]	0.722 (0.010)[e]	0.996	23	78.4	11.5	4.41	0.646
PRX-1	0.609 (0.055)	0.745 (0.026)	0.995	20	72.7	12.5	4.06	0.698
PRX-2	0.633 (0.068)	0.730 (0.031)	0.992	20	91.0	14.1	4.30	0.665
PRX-3	1.091 (0.054)	0.627 (0.027)	0.993	20	330	25.1	12.3	0.940
PRX-4	0.973 (0.048)	0.687 (0.024)	0.996	19	210	25.2	9.40	1.08
PRX-5	1.325 (0.035)	0.614 (0.018)	0.997	20	707	49.1	21.1	1.47
PRX-6	1.497 (0.045)	0.559 (0.024)	0.993	20	1180	55.8	31.4	1.49

(b) Desorption Isotherm Parameters and Calculated Hysteresis Indexes

sorbent	desorption parameters				apparent hysteresis index	
	$\log K_F$	n	R^2	N	$C_e = 1\ \mu g/L$	$C_e = 100\ \mu g/L$
original soil	0.658 (0.033)	0.739 (0.018)	0.990	19	0.03	0.12
PRX-1	0.755 (0.057)	0.729 (0.032)	0.992	20	0.40 (0.24)[f]	0.30 (0.22)
PRX-2	0.674 (0.078)	0.742 (0.043)	0.986	20	0.10 (0.25)	0.16 (0.26)
PRX-3	1.134 (0.070)	0.628 (0.040)	0.984	20	0.10 (0.21)	0.11 (0.21)
PRX-4	1.024 (0.056)	0.715 (0.032)	0.992	19	0.13 (0.18)	0.28 (0.20)
PRX-5	1.262 (0.053)	0.676 (0.031)	0.991	20	−0.14 (0.12)	0.15 (0.16)
PRX-6	1.451 (0.054)	0.606 (0.033)	0.988	20	−0.10 (0.14)	0.12 (0.17)

[a] Units in $(\mu g/g)/(\mu g/L)^n$. [b] Number of observations. [c] Calculated using the listed Freundlich isotherm parameters and the carbon values from Table 2. [d] 95% confidence interval for $\log K_F$. [e] 95% confidence interval for n. [f] 95% confidence interval for hysteresis index (propagated).
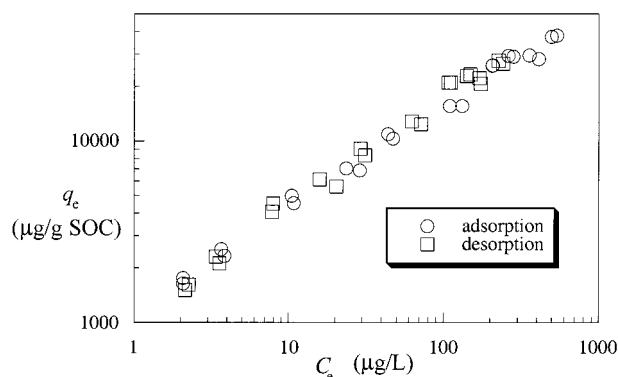

FIGURE 7. Organic carbon normalized phenanthrene sorption and desorption isotherms for Chelsea soil pre-extracted 10 h by 250 °C liquid subcritical water (PRX-6).

sorbents such as shales that exhibit highly nonlinear isotherms for HOCs are also characterized by sorption—desorption hysteresis (14–16). Interestingly, the data presented in Figure 7 show that we have generated a sorbent with a nonlinear isotherm (Freundlich n value 0.56) without measurable hysteresis. Our previous work (16) postulated that entrapment or hindered diffusion within the layers of condensed aromatic carbon matrixes of geologically mature kerogens is one possible mechanism responsible for desorption hysteresis. The aromatic fractions of the organic matter in the pre-extracted Chelsea soil, however, may not have been as densely packed as those of typical shale kerogens

because they were exposed or formed rapidly in the subcritical water rather than condensing over geological time. The fact that the isotherm data for the sample extracted for 10 hours is highly nonlinear but exhibits no desorption hysteresis indirectly supports the hypothesis that HOC entrapment or hindered diffusion occurs within densely compact layers of geologically mature kerogen.

In summary, subcritical superheated water effectively removed polar organic functional groups from Chelsea soil. Mass balances on aromatic carbon strongly suggest that aromatization reactions of the soil organic matter occurred rapidly in this medium. These alterations significantly impacted subsequent sorption equilibria for phenanthrene, a representative HOC. Organic carbon normalized distribution coefficients increased by over an order of magnitude for soil extracted with 250 °C liquid water for 10 h. Furthermore, nonnormalized K_D increased almost an order of magnitude under the same conditions even though half of the soil organic carbon was removed. In fact, the capacity and nonlinearity of phenanthrene sorption by the altered soil organic matter were strikingly similar to those measured previously for geologically mature kerogens of shales and coals.

Chelsea soil, like most soils, is highly heterogeneous, and it contains only 5.6% carbon by mass. We cannot, therefore, absolutely attribute the observed changes in sorption behavior solely to alterations of the soil organic matter. To better isolate the effects of superheated water on organic matter, a similar study should be conducted with a peat sample that is comprised almost entirely of recently deposited organic materials. Diagenesis-like alterations of such peat

organic matter would support and further develop the tentative conclusions advanced herein.

Acknowledgments

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