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Phenanthrene Sorption by Aliphatic-Rich Natural Organic Matter

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Contaminant sorption, an important process that may limit bioavailability, hinder remediation, encourage environmental persistence, and control mobility in the environment, has been the focus of numerous studies. Despite these efforts, the fundamental understanding of sorptive processes in soil and sedimentary environments has not been resolved. For instance, many have suggested that contaminants, such as polycyclic aromatic hydrocarbons (PAHs), solely interact with aromatic domains of organic matter. Until now, studies have neglected the aliphatic components that are known to be a recalcitrant and significant part of soil and sedimentary organic matter (SOM). In this investigation, the sorption of phenanthrene to several aliphatic-rich SOM samples was measured. The samples included the following: SOM precursors (algae, degraded algae, cellulose, collagen, cuticle, and lignin), two kerogen samples, and a highly aromatic humic acid. All samples were characterized by cross polarization magic angle spinning carbon-13 (CPMAS ^{13}C) NMR and carbon, hydrogen, and nitrogen analysis. Batch experiments demonstrated that the highest organic carbon normalized sorption coefficients (K_{oc} values) were obtained with the Pula kerogen sample (log $K_{oc} = 4.88$) that only contains 6.5% aromatic carbon. Other aliphatic-rich samples, namely the Green River kerogen, degraded algae, and collagen samples produced comparable log K_{oc} values (4.64, 4.66, and 4.72, respectively) to that of the highly aromatic humic acid (log $K_{oc} = 4.67$). Phenanthrene uptake was the least for cellulose and lignin, two major soil components. A comparison of phenanthrene K_{oc} values and paraffinic carbon content revealed a positive correlation ($K_{oc} = 798 \pm 96.1$ * paraffinic carbon (%), $r^2 = 0.56$) and indicates that amorphous polymethylene carbon is an important consideration in phenanthrene sorption. This study establishes that aliphatic SOM domains have a strong affinity for phenanthrene and likely, other PAHs. Therefore, aliphatic structures, that are an important component of SOM, require more attention in the examination of sorption processes in terrestrial and sedimentary environments.

Introduction

One of the primary fates of hydrophobic organic contaminants, such as polycyclic aromatic hydrocarbons (PAHs), in terrestrial and aquatic environments is sorption to natural organic matter. The robust association between contaminants and organic matter often limits passive remedial methods, namely bioremediation, and encourages persistence in the environment. Furthermore, PAHs exhibit toxicity at low concentrations. The environmental problems associated with the presence and persistence of PAHs encourages the fundamental understanding of sorptive processes in soil and sedimentary environments. Once sorption mechanisms are understood, improvements in risk assessment, fate and transport models, and remedial methods can be made. Currently, several hypotheses exist regarding the sorption of PAHs and other nonionic organic contaminants to soil and sedimentary organic matter (SOM) (*1*−*7*). Despite the number of theories, the fundamental physicochemical mechanisms responsible for the sequestration of PAHs are poorly understood (*8*).

The progression of understanding sorption mechanisms has grown from correlations between sorption and organic matter content (*9*) to relationships with specific organic matter structures and domains (*10*−*17*). Several of these studies have indicated that sorbent characteristics, such as polarity or aromaticity can be correlated to and account for differences in sorptive behavior. For instance, sorption of chloro-aliphatic chemicals was reported to be inversely proportional to the amount of oxygen in the sorbents and suggested that the degree of weathering, in cooperation with the amount of organic matter, dictated the extent of sorption (*14*). Other studies have correlated sorption to the polarity index (O+N/C) of the sorbent (*12*). More recently, reports suggest that the condensed aromatic carbon phase (black carbon or soot carbon) governs the sorption and distribution of PAHs in sedimentary organic matter (*7*, *10*, *17*). The growing application of cross polarization magic angle spinning carbon-13 nuclear magnetic resonance (CPMAS ^{13}C NMR) has facilitated conclusions in several investigations that contaminant organic carbon normalized sorption coefficients (K_{oc} values) are linearly or exponentially proportional to the aromatic carbon content of the sorbent (*11*−*13*). Despite the level of detail regarding organic matter characterization and the number of hypotheses put forward in the literature, the majority of sorption studies neglect the aliphatic components of SOM.

The aliphatic components of SOM often persist and are preserved through humification processes (*18*−*24*). The long methylene chains originating from microbial products, plant cuticles and suberin, have been identified in SOM, soil humin, and kerogens (*18*−*24*). In sedimentary environments, where terrestrial organic matter inputs are minimal, these polymethylene chains mainly arise from the residues of algal biomass (*25*−*27*). Differences in the types of polymethylene chains have recently been identified in SOM using solid-state NMR spectroscopy (*28*). Both crystalline and amorphous methylene carbons were detected and can be distinguished based on their chemical shift (33 and 31 ppm, respectively). It was hypothesized that only the amorphous region (31 ppm) was responsible for the uptake of contaminants in soils. There have only been a few reports that demonstrate that aliphatic-rich natural organic matter can sorb appreciable amounts of monoaromatic compounds (*29*), pyrene (*30*), and phenanthrene (*31*). The objective of this study was to examine sorption of phenanthrene, a model PAH compound, to a variety of aliphatic-rich organic matter samples to determine the role of specific aliphatic domains (amorphous and crystalline polymethylenic carbon) in PAH sorption. All samples were analyzed for carbon, nitrogen, and hydrogen

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contents and examined by CPMAS ^{13}C NMR to determine presence and/or relative differences in amorphous and crystalline polymethylene carbon domains. The phenanthrene K_{oc} values and Freundlich parameters were obtained by batch sorption methods.

Experimental Section

Sample Collection. The sample set was comprised of the following: algae (*Botryococcus braunii*), degraded algae, cellulose, collagen, leaf cuticle, lignin, humic acid extracted from a black shale/low grade coal, and two kerogen samples. *Botryococcus braunii* is a common green algae that is found in freshwater, brackish, and saline aquatic environments and is representative of aliphatic, insoluble, nonhydrolyzable, and highly refractory cell wall material (termed algaenan) that contributes to and accumulates in sedimentary organic matter (*25*, *32*, *33*). In this study, fresh algae and algae subjected to aerobic, microbial degradation for 201 days (referred to as degraded algae) were used as sorbents. A detailed description of the growth and degradation of the algae is given in ref *25*. The cellulose, collagen (type II), and lignin (organosolv), which represent terrestrial organic matter precursors, were purchased from Sigma Chemicals (St. Louis, MO) and used as received. The cuticle sample, another type of terrestrially derived organic matter addition, was extracted from mangrove leaves as described by Espelie et al. (*34*). A highly aromatic humic acid sample was included in the sample set for comparison of the sorptive capability of aliphatic-rich biopolymers. This humic acid was isolated from a weathered black shale that contained inclusions of coal, sampled along the banks of the Blackmud Creek, located south of Edmonton, Alberta, Canada. The humic acid was isolated with the conventional sodium hydroxide extraction method (*35*). Details of the extraction procedure and characteristics of this humic acid are described in detail by Salloum et al. (*36*). The humic acid sample was altered by a chemical oxidation procedure with sodium hypochlorite to reduce the aromatic content and enhance the aliphatic structures. This treatment breaks the rings of uncondensed aromatic carbon, namely those arising from lignin (*37*). Both the humic acid and the chemically oxidized humic acid were used in the sorption experiments. The first kerogen sample was obtained from Pula, Hungary and is an unique example of a highly aliphatic, Pliocene age kerogen. A complete description and characterization of the Pula kerogen can be found in Derenne et al. (*38*). The second kerogen sample was acquired from the Green River formation in Wyoming. This kerogen is also rich in paraffinic carbon and contains organic matter that has had a large amount of microbial inputs (*39*, *40*). All sorbents were ground to pass a 106 μm sieve prior to batch sorption experiments.

Elemental Analysis and CPMAS ^{13}C NMR. Carbon, hydrogen, and nitrogen analysis was conducted on a Carlo-Erba NA 1500 Series 2 Elemental Analyzer (CE Elantech, Inc., Lakewood, NJ). The carbon, hydrogen, and nitrogen contents along with the H/C atomic ratio are listed in Table 1. The CPMAS ^{13}C NMR spectra were acquired on a Bruker Avance 300 MHz NMR spectrometer, equipped with a 4 mm H-X MAS probe, using the standard ramp-CP pulse program (*41*). Approximately 100 mg of sample was packed into a 4 mm zirconium rotor with a Kel-F cap. The acquisition parameters were as follows: spectral frequency of 75 MHz for ^{13}C and 300 MHz for ^{1}H, spinning rate of 13 kHz, ramp-CP contact time of 2 ms, 1 s recycle delay, and line broadening of 50 Hz. Chemical shifts were calibrated against those of an external standard (glycine). The spectra were integrated into the following chemical shift regions: paraffinic carbon (0−50 ppm); substituted aliphatic carbon including alcohols, amines, carbohydrates, ethers, methoxyl and acetal carbon (50−110 ppm); aromatic and phenolic carbon (110−165 ppm); and carboxyl and carbonyl carbon (163−215 ppm) (*42*, *43*).

TABLE 1. Elemental Analysis and Atomic Ratios of Sorbents

sample	carbon (%)	hydrogen (%)	nitrogen (%)	H/C
algae	55.4	7.96	3.05	1.71
degraded algae	58.3	8.99	3.86	1.83
cellulose	44.4	6.2	0	1.66
collagen	56.0	7.73	12.5	1.64
cuticle	52.4	6.96	0.81	1.58
lignin	69.6	5.79	0	0.99
humic acid	60.4	4.59	1.42	0.90
oxidized humic acid	52.7	3.09	0.97	0.70
Green River kerogen	35.8	2.74	0.88	0.91
Pula kerogen	66.7	9.52	0.68	1.70

Phenanthrene Sorption. Batch phenanthrene sorption experiments were performed as described in Salloum et al. (*36*). Briefly, an aliquot from a concentrated methanol stock of phenanthrene (>98%, ACROS Chemicals) was dissolved in a solution containing 5 mM $CaCl_2$ and 0.01 mM $HgCl_2$ to prevent biological degradation of the sorbate without causing significant changes to the organic matter chemistry (*44*). Methanol concentrations were always less than 0.1% of the total solution volume to avoid cosolvent effects (*45*). Aqueous solutions (25 mL) of varying concentration of phenanthrene (0.2−1.0 mg/L) were added to SOM samples previously weighed into 25 mL Corex II (Fisher Scientific) glass centrifuge tubes. The amount of sample in each tube corresponded to a sample-to-solution ratio that would result in 20−80% uptake of phenanthrene. Five replicates of each starting concentration were assembled, for a total of 25 measurements per isotherm. The tubes were sealed with Teflon lined screw caps and then placed on an agitator (150 rpm) for 48 h at 25 °C (preliminary tests indicated that apparent equilibrium was reached before this time). The tubes were then centrifuged (4000×g for 10 min), and a 2 mL aliquot of the supernatant was removed for quantitative analysis of phenanthrene. Phenanthrene concentrations were measured with a Waters 2690 High Performance Liquid Chromatograph (HPLC) fitted with a Waters 996 photodiode array detector and Supelcosil LC-PAH reverse-phase column (25 cm × 2.1 mm × 5 μm; Supelco, Bellefonte, PA). Injection volumes of 10 μL, a mobile phase of 80% acetonitrile/20% water with a flow rate of 0.25 mL/min, and an absorbance wavelength of 247 nm were used to determine phenanthrene concentration. Phenanthrene uptake to the glass walls of the centrifuge tubes was found to be less than 0.5%. Hence sorption was calculated by difference. Sorption distribution coefficients (K_d) were calculated from the slope of the linear portion of the isotherm using Origin version 6.0 at 95% confidence. The organic carbon normalized sorption coefficient (K_{oc}) was then calculated by dividing K_d values by the respective fraction of organic carbon (f_{oc}) in the sample (*9*). The Freundlich model ($S = K_f C_e^n$) parameters were fitted using Origin version 6.0. S represents the amount of phenanthrene sorbed per gram of sorbent (expressed in mg/g), C_e is the concentration of phenanthrene remaining in solution (mg/L), and K_f and n are constants (*2*).

Results and Discussion

Sorbent Structural Characteristics. The CPMAS ^{13}C NMR spectra of the aliphatic-rich SOM precursors and of the aged organic matter are displayed in Figure 1, and NMR integration results are presented in Table 2. Of all the samples, the humic acid and lignin contain the most aromatic carbon (42.8% and 41.9%, respectively). The remaining samples are composed of at least 32% of paraffinic carbon and less than 24% of aromatic carbon. The algae sample exhibits a slight signal

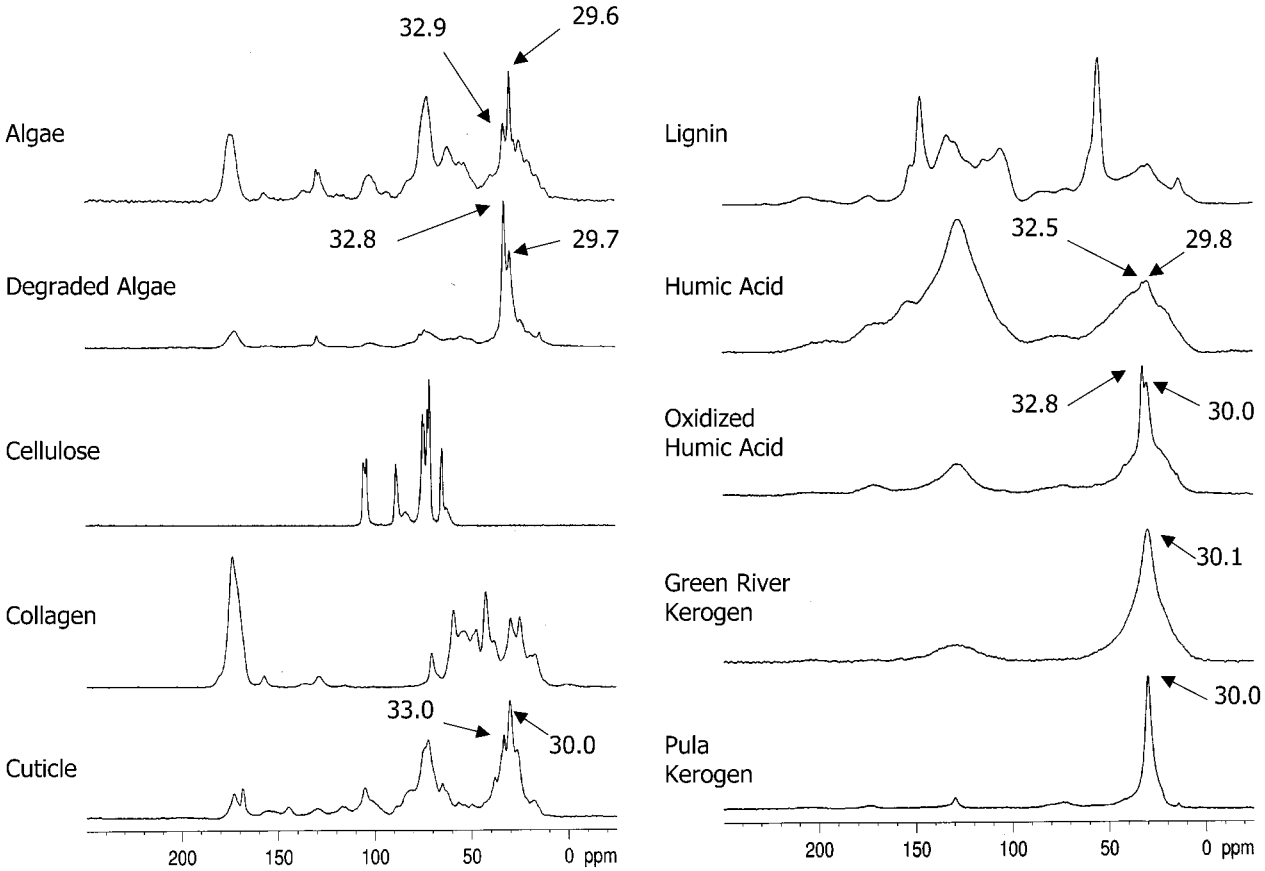

FIGURE 1. Cross polarization magic angle spinning carbon-13 NMR spectra of algae, degraded algae, cellulose, collagen, cuticle, and lignin. Amorphous (~31 ppm) and crystalline (~33 ppm) methylene carbon peaks are labeled where appropriate.

TABLE 2. Cross Polarization Magic Angle Spinning Carbon-13 NMR Integration Results

	relative percentage of carbon as			
sample	paraffinic (0–50 ppm)	O–alkyl (50–110 ppm)	aromatic (110–160 ppm)	carboxyl and carbonyl (160–215 ppm)
algae	32.7	47.2	7.6	12.5
degraded algae	60.3	25.5	5.9	8.3
cellulose	0	100	0	0
collagen	38.9	30.0	3.7	27.4
cuticle	37.0	41.3	13.3	8.4
lignin	19.9	33.4	42.8	3.9
humic acid	21.6	25.4	41.9	11.1
oxidized humic acid	59.6	11.5	23.8	5.1
Green River kerogen	80.7	4.2	13.9	1.2
Pula kerogen	79.5	11.0	6.5	3.0

at 129 ppm for olefinic carbon, however, is primarily composed of carbohydrates (60–72 ppm), methylene carbon (30–35 ppm), and some methoxyl carbon (55–60 ppm) (*42*, *43*). After microbial degradation, the algal residue contains 60.3% methylene carbon (24–32 ppm) and small amounts of carbohydrate carbon (25.5%; 60–72 ppm), olefinic carbon (5.9%; 129 ppm), and carboxyl carbon (8.3%; 172 ppm). Both the fresh and degraded algae contain crystalline and amorphous methylene carbon with the proportion of crystalline carbon increasing with degradation. Detailed, pyrolysis GC-MS studies of algal extracts and algaenan have found that some algal residues can contain C_6–C_7 up to C_{32}–C_{37} *n*-alkanes (ref *32* and references within). Consequently, the assignment of the methylene signals in the CPMAS ^{13}C NMR spectra is consistent with the structural characteristics of *B. braunii*.

The cellulose NMR spectrum contains signals of the hexose ring carbons (56–72 ppm) and the anomeric carbon typical of polysaccharides (105 ppm) (*42*) but is completely devoid of aromatic carbon and methylenic carbon. NMR investigations with cellulose have reported that its structure is predominantly crystalline in nature (*46*, *47*). The collagen spectrum contains a small signal from aromatic carbon but is rich in aliphatic carbon evident from the multitude of signals in the 0–75 ppm region. The strong resonance at 172 ppm can be attributed to amide carbon and/or carboxyl carbon, but considering the proteinaceous nature of this sample and signals from amines that resonate in the 50–110 ppm region, the signal at 172 ppm is likely due to amide carbon. Based on the known structural properties of collagen, the signals in the paraffinic region (0–50 ppm) cannot be assigned to long chain methylene carbons (*48*, *49*).

The structure of plant cuticles has been the subject of several reports. It is understood that cuticle is composed of straight chain, aliphatic biopolymers (*23*, *24*, *50*). Pyrolysis GC-MS analysis has indicated that cuticle components can have *n*-alkane/alkene chain lengths up to C_{33} units in length. ^1H NMR studies with cuticular waxes have identified both amorphous and crystalline regions (*51*). The cuticle spectrum in Figure 1 reveals an aliphatic-rich sample that contains both crystalline and amorphous methylene carbon along with some carbohydrate carbon (60–72 ppm). Also apparent is a small signal from anomeric carbon of polysaccharides (105 ppm) and carboxyl carbon (175 ppm). Lignin, which is an important component of soil organic matter, is rich in aromatic (110–145) and phenolic (145–155 ppm) carbon. The methoxyl carbon signal (56 ppm) is prevalent, and its intensity is consistent with the structural properties of lignin (*52*, *53*). However, the current understanding of lignin structure does not support the presence of long, methylene

TABLE 3. Phenanthrene Sorption Coefficients and Freundlich Model Parameters

sample	K_d (mL/g)	linear r^2	K_{oc} (mL/g)	log K_{oc}	K_f (mg/g)/(mg/L)^n	n	Freundlich r^2
algae	13630 ± 636	0.99	24603 ± 123	4.39	14.94 ± 0.39	0.77 ± 0.03	0.99
degraded algae	26660 ± 230	0.97	45729 ± 228	4.66	26.39 ± 1.47	0.89 ± 0.05	0.99
cellulose	951.8 ± 7.6	0.98	2143 ± 11	3.33	1.01 ± 0.038	0.87 ± 0.08	0.98
collagen	29550 ± 117	0.99	52767 ± 264	4.72	27.21 ± 2.09	0.72 ± 0.06	0.99
cuticle	16468 ± 641	0.99	31429 ± 157	4.50	16.43 ± 0.77	0.84 ± 0.05	0.99
lignin	10627 ± 114	0.97	15269 ± 76	4.18	15.57 ± 0.59	0.67 ± 0.05	0.98
humic acid	28089 ± 845	0.99	46475 ± 232	4.67	20.37 ± 2.47	0.65 ± 0.08	0.96
oxidized humic acid	19166 ± 747	0.99	36355 ± 164	4.56	19.69 ± 0.95	0.78 ± 0.04	0.99
Green River kerogen	15631 ± 770	0.99	43615 ± 262	4.64	16.97 ± 0.09	0.76 ± 0.01	0.93
Pula kerogen	50854 ± 292	0.99	76210 ± 366	4.88	35.48 ± 1.27	0.74 ± 0.02	0.94

chains (*54*). The 19.9% aliphatic carbon (0−50 ppm) can be attributed to unsubstituted branched or terminal CH_3 groups or to coisolated resinous components of wood (*43*, *53*).

The humic acid sample exhibits two broad resonances: the first is attributed to alkyl carbon (0−50 ppm) and the second to aromatic carbon (128 ppm). After oxidation, the aromaticity of the humic acid is reduced from 41.9% to 23.8%. Resolution of methylene carbon (30 and 32.8 ppm) is also apparent after oxidation suggesting that in the whole humic acid, these structural components are masked by the broad resonance from other structures in the aliphatic region. The Green River kerogen sample has been reported to contain long, straight chain aliphatic structures up to C_{35} (*39*, *40*, *55*). The CPMAS ^{13}C NMR spectrum of the Green River kerogen exhibits two main signals at 30.1 and 128.6 ppm. For this sample, the line broadening was reduced from 50 to 25 Hz and 5 Hz to determine if the broadness of the peak was masking a crystalline shoulder. A reduction in the line broadening did not reveal any signals that are consistent with crystalline materials (data not shown). The Pula kerogen sample displays a small signal from aromatic (129 ppm) and carboxylic (172 ppm) carbon but is composed mostly of amorphous methylene carbon (30 ppm). Pyrolysis GC-MS of the Pula kerogen yields a series of C_{27}−C_{31} *n*-alkanes (*38*). Therefore, the signal at 30 ppm is consistent with the presence of polymethylenic carbon.

Comparison of Phenanthrene Sorption with Sorbent Structure. The phenanthrene linear and Freundlich sorption coefficients are listed in Table 3, and the sorption isotherms are plotted in Figure 2. Due to the slight nonlinearity of the higher points in the sorption isotherm, the K_{oc} values were calculated from the first four isotherm points (20 data points in total). The Freundlich model was applied to all the isotherm data points (25 data points in total). The phenanthrene K_{oc} values in Table 3 are in the range of those reported for humic material and soils (*56*, *57*). The phenanthrene K_{oc} values are highest for the Pula kerogen sample and lowest for the cellulose sample. With the exception of cellulose, the phenanthrene log K_{oc} values are within the same order of magnitude, despite the differences in aromatic and aliphatic carbon content. For instance, phenanthrene sorption to the highly aromatic humic acid sample was surpassed by both the collagen and Pula kerogen samples. The Green River kerogen and the degraded algae samples produced phenanthrene K_{oc} values only slightly lower than the highly aromatic humic acid sample. After the aromaticity of the humic acid was reduced by chemical oxidation, the residue, which contained 60% paraffinic carbon, was able to sorb comparable amounts of phenanthrene. The lignin sample, which contains the most aromatic carbon, sorbed more phenanthrene than only the cellulose sample. These data demonstrate that natural organic matter that is rich in aliphatic carbon has the capability to sorb as much or even more phenanthrene than highly aromatic components such as the humic acid and lignin samples used here. Furthermore, the decline in aromaticity of the humic acid sample was not met with an equal decline in phenanthrene sorption suggesting that the paraffinic components of SOM contribute significantly to the sorption of PAHs.

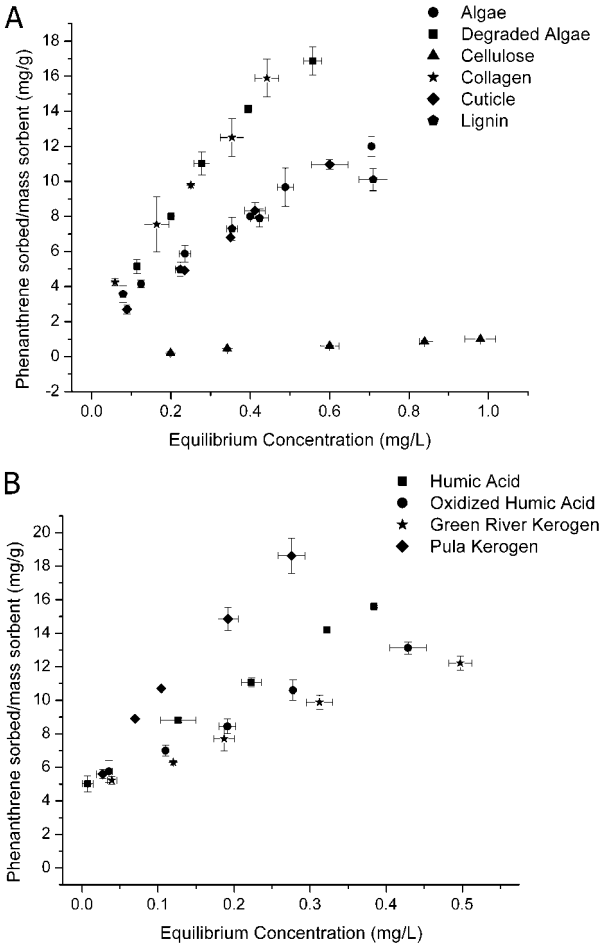

FIGURE 2. Phenanthrene sorption isotherms to organic matter sorbents: (A) natural organic matter precursors and (B) aged natural organic matter.

The sorption nonlinearity, as determined by the Freundlich parameter *n*, varies from 0.65 to 0.89. Both of the aromatic-rich sorbents, the lignin and humic acid, produced the most nonlinearity with *n* values of 0.67 and 0.65, respectively. The predominantly aliphatic samples produced *n* values that range from 0.72 to 0.89, suggesting that the sorption mechanism may differ with these samples. Interestingly, the isotherm linearity of the algae increased after the sample had undergone microbial degradation. This trend was also observed with the humic acid sample. After the aromaticity had been reduced by chemical oxidation, the sorption linearity improved due to enhanced access to mobile polymethylenic domains. These data and the inherent trend

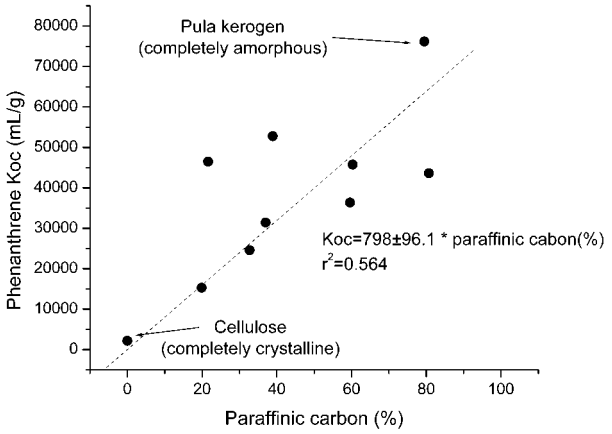

FIGURE 3. Positive correlation between phenanthrene K_{oc} values and paraffinic (0−50 ppm) carbon content of the samples.

suggest that sorption to mobile, aliphatic domains is similar to sorption to "rubbery" rather than "glassy" type carbon (*2*). Furthermore, it also implies that the sorption capacity and mode of sorption to aliphatic and aromatic structures within SOM vastly differ.

A comparison between phenanthrene K_{oc} values and paraffinic carbon content (Figure 3) reveals a general, positive trend between these two variables and can be described by the following equation: $K_{oc} = 798 \pm 96.1$ * paraffinic carbon (%) ($r^2 = 0.56$). This is consistent with the positive correlation with pyrene and sample aliphaticity as reported by Chefetz et al. (*30*). Furthermore, high sorption affinity of nonionic organic contaminants has been reported for highly aliphatic corn leaf residues (*29*) and plant cuticles (*30*). Recently, phenanthrene sorption to humic acids and humin fractions has been correlated to polymethylene-rich domains in SOM (*31*). These reports are few in number in comparison to those that have reported positive correlations between the sample aromatic carbon content and sorption coefficients (*11*−*13*, *58*, *59*). However, it is apparent that there is a level of specificity in sorption to aliphatic organic matter domains. For instance, there is a distinct correlation between phenanthrene K_{oc} values and amorphous methylene carbon. Of the samples studied, the cellulose and lignin samples are devoid of amorphous paraffinic carbon and produced the lowest phenanthrene K_{oc} values. Alternatively, sorbents that contain predominantly or a large amount of amorphous methylene carbon, such as the Pula kerogen sample, produced higher phenanthrene K_{oc} values than the aromatic-rich samples. These observations are consistent with the hypothesis of Hu et al. (*28*) who suggested that sorption of nonionic organic contaminants will be primarily to the amorphous polymethylene structures in humic materials. The phenanthrene K_{oc} value for collagen was notably high, despite the absence of polymethylenic carbon. This has been attributed to the ability for collagen to assemble into a triple-helical structure with hydrophobic domains (*60*). Nonetheless, it is another example sorbent that is a component of SOM, has low aromaticity and high aliphaticity, and is capable of producing high phenanthrene K_{oc} values.

The phenanthrene K_{oc} values and the sorption isotherm linearity increased after the algae had undergone microbial degradation. It is apparent from the CPMAS ^{13}C NMR spectra that after the degradation process, much of the polysaccharides (50−75 ppm) were removed and the proportion of amorphous to crystalline polymethylene carbon decreased. Despite the decrease in amorphous methylene carbon, the K_{oc} increased. Similarly, the removal of a large portion of the aromatic structures in the humic acid did not result in a large reduction in the log K_{oc} value. The broad "peak" in the humic acid CPMAS ^{13}C NMR spectrum from 0 to 50 ppm became more resolved after chemical oxidation and revealed the presence of polymethylenic structures that were previously masked by the signals from other structures. Because the K_{oc} value did not decline significantly after oxidation, it suggests that the polymethylenic structures were involved in phenanthrene sorption before and after oxidation. Moreover, the overall trend of the data imply that although polymethylenic structures can sorb appreciable amounts of phenanthrene, they may be physically constrained by other SOM structures, such as lignin, cellulose, etc., and may not always be physically accessible or may not be able to out compete other SOM structures. Other reports have indicated that sorption to organic matter may be regulated by the physical accessibility to specific structures rather than the structures themselves (*36*) and is consistent with the observations presented here. For instance, it is clear that amorphous polymethylenic domains can sorb substantial amounts of phenanthrene. However, the role and distribution of these domains in conjunction with other structures in SOM needs to be evaluated before mechanistic information of PAH sorption can be completely understood.

The results of this experiment have several environmental implications. It is well established that aliphatic biopolymers are a recalcitrant and integral part of SOM (*18*−*24*). Furthermore, organic matter in sedimentary environments and some kerogen deposits, that lack terrestrial organic matter additions, contain predominantly aliphatic moieties. Consequently, it is important to consider the role of aliphatic structures in the sorption of nonionic, hydrophobic organic contaminants. Furthermore, these results undermine reports that implicate aromatic domains, namely black carbon, as the sole SOM moiety that regulates sorption of PAHs (*7*, *10*, *17*). A recent report using high-resolution magic angle spinning (HR MAS) ^{1}H NMR on a forest soil sample indicated that only polysaccharide, peptide, and cuticular structures are visible at the soil−water interface, when the soil is wetted with D_2O (*61*). When the sample was wetted with DMSO-d_6, a penetrating solvent that breaks up hydrogen bonds, the aromatic structures became NMR visible. Simpson et al. (*61*) concluded that aromatic organic matter structures do not exist at the soil−water interface but are buried within soil colloids. Several other studies that examined sorption of contaminants to SOM conclude that not all organic matter structures are directly participating in sorption reactions due to the regulation of physical conformation by soil minerals (*36*, *62*, *63*). If aliphatic structures are the components of organic matter that are readily accessible on the surface of soil colloids, then the application of bulk organic matter properties, such as aromatic or black carbon content, to determine and describe the sorptive capacity may not be appropriate. Furthermore, it is apparent that aliphatic structures require more attention when considering the uptake, sequestration, and bioavailability of organic contaminants in soil and sedimentary environments simply due to their presence, persistence, and capability to sorb appreciable amounts of phenanthrene.

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