

Pyrene Sorption by Natural Organic Matter

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Sorption of pyrene on various types of natural organic matter (NOM) varying in chemical composition (e.g. high aliphaticity or aromaticity) was examined in batch sorption studies. The NOM samples (cuticle, humin, humic acid, degraded lignin, peat and lignite) were characterized by elemental analyses and solid-state ^{13}C NMR spectra. Previous studies on polycyclic aromatic hydrocarbons (PAHs) sorption on soils and sediments led to the conclusion that aromatic component of the NOM determines the binding of nonionic compounds and that the polarity of the NOM reduces the binding coefficient of the aromatic NOM moieties. In this study we tested the hypothesis that aliphatic moieties of NOM derived from soils or sediments can contribute significantly to the binding of PAHs in aqueous media. Cuticle and a humin sample from an algal deposit exhibited the highest distribution coefficients (K_{oc}). Both samples were rich in aliphatic structures and had very low aromaticity (4.6 and 8.8% for cuticle and humin samples, respectively). A positive trend was observed between the K_{oc} level and the aliphaticity of the NOM, calculated from the ^{13}C NMR spectra. This study demonstrates that aliphatic NOM compounds significantly sorb pyrene in aqueous solution, thus leading to the conclusion that the contribution of these groups to the sorption of aromatic nonionic pollutants in complex NOM matrices can be significant.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of compounds consisting of more than two benzene rings fused in a linear, angular, or clustered arrangement. PAHs originate from various sources. Geochemical processes yield PAHs when natural organic matter (NOM) is exposed to high pressure and temperature. Anthropogenic practices, such as industrial processing, petroleum spills, and incomplete combustion of fuel, also contribute to high levels of PAHs in the environment. The fate of PAHs in soils and sediments is related to their solubility, bioavailability, biodegradability, and sorption/desorption mechanisms (1–4).

Sorption of nonionic organic compounds by soils and sediments has been shown to be controlled by the mineral

type and soil organic matter (OM) content (5, 6). However, strong dipole interactions between the mineral surfaces and water decreases the mineral surface sorption of PAHs and increases the sorption effects by OM (7). Onken and Traina (6) reported that the sorption of pyrene and anthracene to humic acid (HA)–mineral complexes increased as the fraction of organic carbon ($\times a_{6_{oc}}$) in the complexes increased. Consistent C-normalized distribution coefficients (K_{oc}) were reported to vary between samples due to different origin and maturity of OM (8). Previous studies have shown that the K_{oc} values calculated for the binding of pyrene to humic substances were strongly correlated with the content of aromatic C moieties measured by ^{13}C NMR (9, 10). Kile et al. (11) reported that the average K_{oc} calculated for carbon tetrachloride and 1,2-dichlorobenzene (both nonionic compounds) are twice as high for sediments than for soils even though the samples do not differ significantly in their aromatic C content. These authors concluded that the polar C content (aliphatic C plus carboxyl and carbonyl C) negatively affects sorption of nonionic organic compounds to OM. Chiou et al. (12) suggested that the higher partitioning of nonionic compounds to aromatic rather than aliphatic components of NOM occurs, in accordance with their higher solubility in an aromatic rather than aliphatic solvent (benzene and *n*-hexane, respectively).

Although it is well documented (13) that NOM predominantly controls sorption of PAHs and other nonionic compounds in soils and sediments, the role of its composition, nature, and physical conformation in determining the sorption coefficient requires further corroboration. Several recent publications assigned the control of sorption properties of nonionic compounds on NOM to its aromaticity (11–13). In this study, we focused on the contribution of both aliphatic and aromatic moieties of various types of NOM to the sorption behavior of PAHs. Sample characterization was performed using elemental analysis and cross polarization magic angle spinning (CPMAS) ^{13}C NMR. Batch sorption experiments were employed to study the interaction of pyrene with six different types of NOM samples representing a wide range of chemical structures.

Experimental Section

Samples. Samples of widely differing compositions of OM were chosen for this study to represent NOM likely to be found in soils or sediments. The samples chosen exhibited a wide range of aromaticity and aliphaticity. The samples were as follows: (1) Degraded lignin—originating from a Douglas Fir log (*Pseudotsuga menziesii*), sampled in Mount Rainier, Washington and was described previously (14). (2) Humin—extracted from an algal sapropel formed in a lake (Warwick pond, Bermuda). This sample was collected in 1982 by coring the shallow lake, and it represents the lower (15–30 cm) section of the core. The humin was extracted according to the method described by Hatcher et al. (15). (3) Peat—was collected from a core of a sawgrass peat from The Everglades, Florida. The sample originated from a depth of 100 cm in the peat, below the zone of biodegradation. (4) HA—extracted from The Everglades peat sample according to the method described by Hatcher et al. (15). (5) Cuticle—which was extracted from tomato according to the method described by Espelie et al. (16). (6) Lignite—obtained from coalified log collected from the Patapsco Formation, (Cretaceous), Landsdowne, MD (17).

Sorption Experiments. Pyrene sorption experiments were conducted in triplicate, in 500 mL round-bottom flasks. Twenty milligrams of the NOM sample were mixed with 500

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mL of HPLC-grade water (J. T. Baker, Phillipsburg, NJ) which were acidified to pH 4.5 using 6 M HCl. HgCl₂ was added to a concentration of 0.1 mM aiming to eliminate microbial activity. The flasks were continuously mixed on a shaker in the dark, at 150 rpm at room temperature. After 48 h of mixing, 12.5 μ L of a pyrene (Aldrich Chemicals, Milwaukee, WI) stock solution (1 mg/mL in methanol) was added to each flask. Pyrene concentration was progressively increased by adding doses of 12.5 μ L of the pyrene stock solution to each flask every 48 h. An incubation period of 48 h was chosen after a preliminary kinetic experiment was conducted for 96 h. The data revealed a concentration plateau after 48 h. Due to its low final concentration (<0.1% v/v) the carrier solvent (methanol) was assumed to have no effect on the sorbate-sorbent interaction (18). Before adding a new dose of pyrene, flasks were allowed to settle down for 4–5 h, and then subsamples (1 mL) were taken from the top layer of the solution for pyrene equilibrium concentration determination. The amount of sorbed pyrene was calculated by quantifying the pyrene loss in the solution. Pyrene was quantified using high performance liquid chromatography (HPLC, Waters 2690, Waters, Milford, MA) equipped with a fluorescence detector (Waters 474 Scanning fluorescence detector) and a reverse-phase column (25 cm \times 2.1 mm 5 μ m; Supelcosil LC-PAH, Supelco, Bellefonte, PA). The elution gradient was 60% acetonitrile/40% water to 80% acetonitrile/20% water, at 3 min and to 100% acetonitrile at 18 min with a flow rate of 0.25 mL/min. Pyrene concentration was determined using an excitation wavelength of 260 nm and emission wavelength of 374 nm. The amount of pyrene was determined by injecting 10 μ L of samples with external pyrene standards.

Recovery of Sorbed Pyrene. After the sorption experiments were performed, the aqueous solution was decanted, and the remaining NOM sample was freeze-dried. Then, each NOM sample was lipid-extracted for pyrene recovery by adding 20 mL of methylene chloride/methanol (2:1 v/v) solution to the freeze-dried NOM sample in 50 mL Teflon centrifuge tubes (Fisher Scientific, Pittsburgh, PA). The tubes were sonicated for 2 min (pulse mode, 20s; Branson Sonifier 250) and then mixed on a shaker (200 rpm) for 24 h. The supernatant was separated by centrifugation (12 000 rpm for 15 min), concentrated under a flow of N₂ gas, and injected to an HPLC system (Waters 2690) to determine pyrene concentration. Pyrene concentration was determined using absorbance at a wavelength of 254 nm with photodiode array detector (Waters 996 PDA detector). Recoveries of the total pyrene mass for the different samples were 85–92%.

Cross Polarization Magic Angle Spinning (CPMAS) ¹³C NMR Spectroscopy. CPMAS ¹³C NMR spectra were obtained using a Bruker DPX 300 MHz NMR-spectrometer (Bruker Analytic GmbH, Germany). The spectrometer operates at a ¹H frequency of 300 MHz and a ¹³C frequency of 75.5 MHz. The experimental parameters were as follows: contact time of 2 ms; recycle delay time of 1 s; sweep width of 27 kHz (368 ppm); and line broadening of 100 Hz. Freeze-dried NOM samples were placed in a 4 mm rotor and spun at a frequency of 13 kHz at the magic angle (54.7° to the magnetic field). The cross polarization (CP) ramp method was used to obtain quantitative spectra at this field (19). To obtain spectra that would be quantitatively representative of the structural components of the sample, an optimal contact time had to be determined. The optimum contact time was determined by analyzing the peak intensity of HA sample at various contact times (0.1–15 ms) with ramp CPMAS (20). A contact time of 2 ms was chosen to be optimal time, because it more accurately reproduces a spectrum similar to that of the Bloch decay.

The ¹³C NMR spectra were integrated according to the following regions: 0–50 ppm, paraffinic carbon; 50–112 ppm, alkyl-O or C–O, C–N bonds as in carbohydrates,

TABLE 1. Elemental Analyses and C/N, H/C, and O/H Ratios of the Studied Samples

	% C ^a	% H ^a	% N ^a	% O ^a	C/N ^b	O/C ^b	H/C ^b
cuticle	60.7	8.6	1.0	29.7	71.2	0.4	1.7
humic acid	50.1	4.5	3.7	41.6	15.7	0.6	1.1
humins	47.3	6.6	3.7	42.4	14.9	0.7	1.7
degraded lignin	55.4	5.3	0.1	39.2	523.9	0.5	1.1
lignite	59.8	4.4	0.0	35.8	2634.0	0.4	0.9
peat	47.5	5.3	2.8	44.5	20.1	0.7	1.3

^a Values represent the mean of triplicate measurements with a coefficient of variation less than 5%. ^b Atomic ratio.

alcohols, ethers, and amines; 112–145 ppm, aromatic C; 145–163 ppm, phenolic C; and 163–190 ppm, carboxyl, ester, and amide C. The region 0–112 ppm was calculated as aliphatic C and 112–163 ppm as aromatic C. Total aromaticity was calculated by expressing aromatic C as a percentage of the aliphatic plus aromatic C; the total aliphaticity was calculated by expressing aliphatic C as a percentage of the aliphatic and aromatic C (15, 21).

Elemental Analysis. Elemental analyses of the NOM samples were performed in triplicates using an EA 1108 Elemental Analyzer (Fisons Instruments, Milan).

Data Analysis. Pyrene sorption was calculated based on the difference in solution concentration and the total amounts of pyrene added to the solution. Slopes of sorption isotherms (K_{om}) were calculated for the linear part of each isotherm (0–0.02 ppm for the cuticle, humin, lignite, and lignin samples and 0–0.8 ppm for the peat and HA samples). Values of K_{oc} were calculated from the K_{om} by normalizing to the C level of each type of OM (3 replicates). The Freundlich $1/n$ parameter was calculated from the logarithmic form of the equation $q = K_d C^{1/n}$ where q is the amount of pyrene sorbed per unit weight of the NOM, C is solution concentration, K_d is the distribution coefficient, and n is a correction factor (22, 23).

Results and Discussion

As reported previously, the chemical nature of OM is perceived to be one of the major factors controlling PAHs sorption to soils and sediments (9, 10, 12, 13). The importance of aromatic rather than aliphatic moieties of OM in the sorption process of nonionic compounds has been stressed in these studies. In the present research we tested this hypothesis using a series of NOM samples comprised of different levels of aromaticity and aliphaticity.

The use of CPMAS ¹³C NMR spectroscopy along with elemental analysis provides useful information on the chemical properties of the various NOM samples and their effects on pyrene sorption. Elemental composition and atomic ratios of the studied NOM samples are presented in Table 1. The cuticle exhibited the highest C content and H/C ratio. Lignite and degraded lignin samples exhibited a very low content of N and H/C ratios close to 1. The humin exhibited a high H/C ratio suggesting high aliphaticity.

CPMAS ¹³C NMR spectra of the NOM samples and the C-containing functional group contents are presented in Figure 1 and Table 2, respectively. The CPMAS ¹³C NMR spectrum of the degraded lignin exhibited major peaks at 55 ppm (methoxy carbons), 62 and 75 ppm (alkyl-O carbons), 115 ppm (protonated aromatic carbons), 131 ppm (C-substituted aromatic carbons), and 147 ppm (C3 and C5 in etherified phenolic guaiacyl units). The degraded lignin consisted mainly of lignin composed of guaiacyl structures as had been previously characterized by Hatcher et al. (24). The total aromaticity calculated for the degraded lignin was 40.2%. The CPMAS ¹³C NMR spectrum of the lignite exhibited major peaks at 36 ppm (methylene carbons), 55 ppm, 115

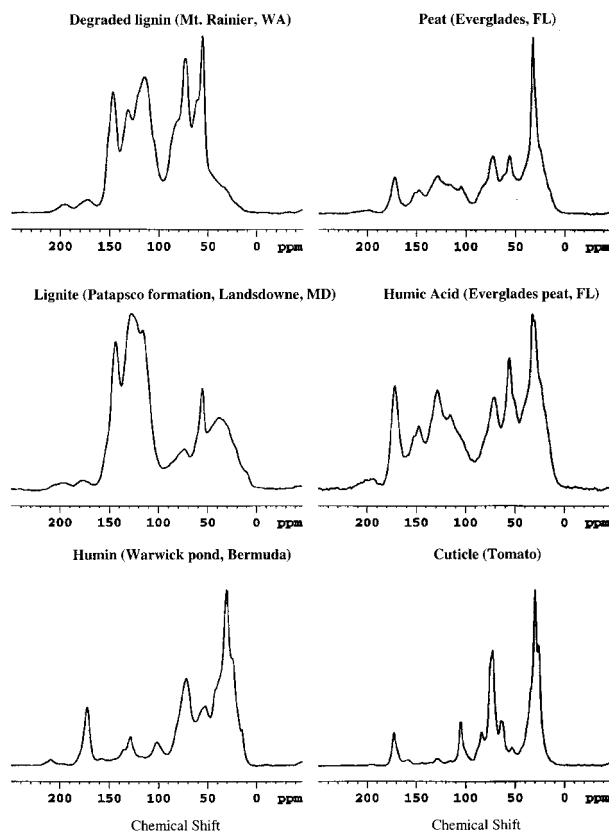


FIGURE 1. Cross polarization magic angle spinning (CPMAS) ^{13}C -nuclear magnetic resonance (NMR) spectra of natural organic matter.

ppm, 127 ppm (C-substituted aromatic carbons), and 144 ppm (catechol-like structures). Total aromaticity calculated for the lignite was 54.5%. The CPMAS ^{13}C NMR spectrum of the Warwick pond humin exhibited a high content of aliphatic compounds (total aromaticity as low as 8.8%) and had major peaks at 30 ppm (methylene carbons), 72 and 105 ppm (carbohydrate carbons), and 128 and 172 ppm (carboxyl/amide carbons). A spectrum of this nature is characteristic of sedimentary NOM derived from algal sources (15). The CPMAS ^{13}C NMR spectrum of the peat sample exhibited major peaks at 32 ppm (methylene carbons), 55 ppm, 72, 130, and 172 ppm. The total aromaticity calculated for the peat was 21.9%. The CPMAS ^{13}C NMR spectrum of the peat HA revealed the following composition: aliphatic moieties (32 ppm), lignin-type structures (55 and 150 ppm), carbohydrates (72 ppm), nonpolar aromatic compounds (115 and 130 ppm), and amide or carboxylic acid-containing compounds (172 ppm). Total aromaticity calculated for the HA was 29.6%. The CPMAS ^{13}C NMR spectrum of the cuticle exhibited major peaks at 26 and 29 ppm (long-chain aliphatic structures) and carbohydrate residues (72, 105 and 172 ppm). Cuticle in plants is composed mainly of polyester-like plant polymers called cutin. The total aromaticity calculated for the cuticle was 4.6%. The wide spectrum of chemical properties of the NOM chosen for this research provided a unique opportunity to study the significance of specific moieties to pyrene sorption.

Sorption isotherms of pyrene (in water) to NOM samples are presented in Figure 2. Three samples (peat, HA, and cuticle) exhibited linear isotherms throughout the measured range. The calculated distribution coefficients (K_{om}) for these isotherms were 41 100, 24 400, and 301 000 for the peat, HA, and cuticle, respectively. The C content and the K_{oc} levels were 47.5, 50.1, and 60.7%, and 86 400, 48 700, and 495 900 for the peat, HA, and cuticle, respectively. The $\log K_{\text{oc}}$ levels calculated for these samples (Table 3) are in the range

predicted for $\log K_{\text{oc}}$ based on the pyrene K_{ow} (octanol–water partition coefficient (12)). The curve types, defined by Sposito (22), and the high K_{oc} values suggest that partitioning is the main mechanism of interaction between the solvent (water) and the sorbent (NOM). It is worth noting that the K_{oc} calculated for the cuticle is 6.4 and 3.6 times higher than the K_{oc} values calculated for peat and humin, respectively. The sorption isotherms for peat and HA fit C-type curves, while the cuticle isotherm fits a H-type curve (note the expanded x axis; Figure 3). H-type curves indicate very strong sorbate–sorbent interactions (22, 23). This condition is achieved by highly specific bonding interactions or by significant van der Waals interactions. The $\log K_{\text{oc}}$ calculated for the HA in our experiment is higher than that reported for pyrene sorption to a Na-montmorillonite–HA complex ($\log K_{\text{oc}} = 4.03\text{--}3.92$) (11). The K_{oc} value of the HA is lower than the one reported for Aldrich HA but higher than that determined for the Suwannee River HA (150 000 and 21 380, respectively) (10). These differences imply that the source and composition of the HAs are of great importance to their capacity to sorb PAHs.

Nonlinear (L type) isotherms were exhibited by the degraded lignin, lignite and humin samples (Figures 2 and 3). The calculated K_{om} for these isotherms were 77400, 66500 and 148300 for degraded lignin, lignite, and humin, respectively. The C content of the degraded lignin, lignite, and humin were 55.4, 59.8, and 47.2%, respectively. $\log K_{\text{oc}}$ and $1/n$ Freundlich values are presented in Table 3. None of these curves exhibited an asymptote typical for Langmuir type of isotherms.

Chiou et al. (12) reported that sediments rich in aromatic C exhibited higher K_{oc} values than soils, noting that differences in aromaticity do not provide a convincing explanation as to the differences between the observed K_{oc} values. The authors concluded that the polar group content (O-aryl and carboxyl C) had a significant negative impact on the value of K_{oc} . A similar conclusion was drawn by Chin et al. (10), Gauthier et al. (9), and Ganaye et al. (25), namely that an increase in aromaticity of HAs results in increased binding of nonionic compounds. Moreover, Chin et al. (10) reported that the higher the aliphaticity of fulvic acids the less capable they are to bind pyrene. Our data contrast with these conclusions as we demonstrate that aliphatic structures (including a high fraction of polar C groups) do have a significant impact on K_{oc} . The cuticle sample that consisted of a very low level of aromatic structures exhibited the highest K_{oc} (495 900) and a H-type isotherm curve. The humin, having the second highest aliphaticity level, exhibited the second highest K_{oc} value (313 800). These data show the importance of nonaromatic structures (mainly paraffinic and O-alkyl C) to sorption processes of PAHs to NOM.

Soil OM was reported to contain long-chain fatty acids and alkanes, which derived from plant cuticular materials (26, 27). In sediments, long-chain aliphatic structures derived from refractory components of algae can enhance NOM aliphaticity (28). Guthrie et al. (29) studied the fate of ^{13}C -labeled pyrene during 60 days of aerobic incubation with a marine sediment from New Orleans, LA. The association of pyrene with the NOM over the course of time showed an increasing amount of pyrene attached to the humin fraction. The CPMAS ^{13}C NMR spectra suggested noncovalent interaction between pyrene and humin. The humin sample used in the present study and the humin fraction reported by Guthrie et al. (29) exhibited high aliphaticity. These data support our hypothesis that aliphatic structures of NOM have a significant impact on pyrene sorption.

The K_{oc} value calculated for the lignin was higher than that calculated for the lignite although higher aromaticity was calculated for the lignite sample. Both samples have polar aromatic structures (guaiacyl and catechol for lignin

TABLE 2. Distribution of Natural Organic Matter C-Containing Groups as Determined by CPMAS ¹³C NMR as a Percent of Total Carbon

C-containing group	chemical shift (ppm)	samples					
		cuticle	humic acid	humins	degraded lignin	lignite	peat
alkyl	0–50	45	31	48	7	19	39
alkyl-O	50–112	45	32	35	50	25	34
aromatic	112–145	3	19	6	30	44	16
phenolic	145–163	5	7	2	9	9	5
carboxyl	163–190	1	9	8	2	2	6
carbonyl	190–215	0	1	1	1	1	1
aromaticity ^a		4.6	29.6	8.8	40.2	54.5	21.9
aliphaticity ^b		95.4	70.4	91.2	59.8	45.5	78.1

^a Aromaticity was calculated by expressing aromatic C (112–163 ppm) as percentage of the aliphatic and aromatic regions (0–163 ppm).
^b Aliphaticity was calculated by expressing aliphatic C (0–112 ppm) as percentage of the aliphatic and aromatic regions (0–163 ppm).

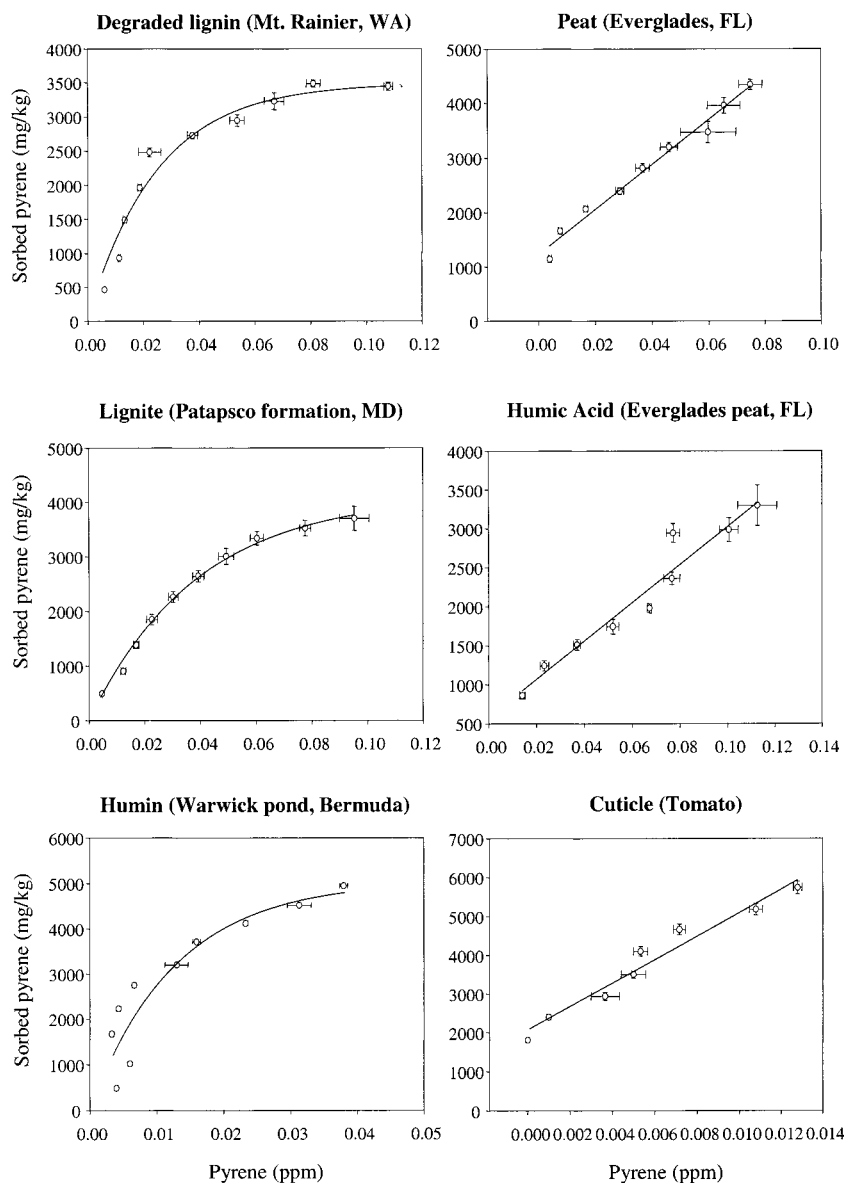


FIGURE 2. Sorption isotherms of pyrene to natural organic matter at room temperature (bars represent standard deviation).

and lignite, respectively). But, the lignite sample contains more paraffinic C moieties and is known to have a microporous structure (30). These micropores can trap small size molecules such as pyrene and therefore can develop none-linearity sorption isotherm. Thus, the mechanism involved in pyrene sorption by lignite is likely to originate from a combination of factors due to the presence of

refractory aliphatic structures, aromatic components, and a micropore structure.

The HA exhibited higher aromaticity than the peat (29.6 vs 21.9%, respectively), yet the K_{oc} exhibited by the peat sample is higher than that of the HA. It seems that higher polarity of the HA resulting from higher levels of carboxylic C and phenol functional groups resulted in a lower binding

TABLE 3. Linear Regression Coefficients, Freundlich 1/n, and Log K_{oc} Values for Pyrene Isotherms with Different Natural Organic Matter

sample	log (K_{oc})	r^2	Freundlich		nonlinear r^2 $y = a \times (1 - e^{-bx})$
			1/n	r^2	
cuticle	5.70	0.89	0.65	0.60	
humic acid	4.69	0.84	0.82	0.82	
humins	5.50	0.61	0.65	0.62	0.85
degraded lignin	5.15	0.87	0.63	0.83	0.92
lignite	5.05	0.92	0.68	0.94	0.93
peat	4.94	0.85	0.69	0.89	

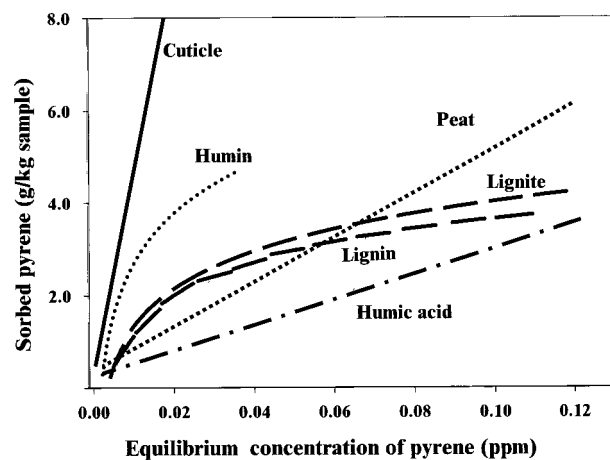


FIGURE 3. Regression curves of the sorption isotherms presented in Figure 2.

capacity. The O-aryl C containing group has little or no effect on the sorption behavior as is observed for the HA, humins, and peat samples, all having almost the same O-aryl level (32–35%) yet highly differing K_{oc} values. This is contrast to observation made by Kile et al. (31).

A positive trend of dependence was observed between the aliphaticity of the OM and log K_{oc} values obtained from the sorption isotherms (Figure 4a), whereas inverse relationship was observed between the log K_{oc} and aromaticity from the sorption isotherms (Figure 4b). Furthermore, when we excluded the K_{oc} values of the lignin and lignite from the plots of K_{oc} vs both aromaticity and aliphaticity the correlations coefficients increased dramatically (Figure 4c,d). The lignin and lignite samples have a similar chemical nature, yet they differ from the other samples (e.g. very high C/N ratio). All other samples (except of the cuticle) are part of soil or sediment humic substances (HS). This suggests that NOM originating from different sources (e.g. soil, sediment, and aquatic) may exhibit different relationship between their chemical composition and PAHs sorption.

The positive trend observed in this study between aliphaticity and K_{oc} values for pyrene emphasizes the importance of the aliphatic moieties in the sorption process. These observations differ from the positive correlation plots reported for log K_{oc} vs aromaticity and for the inverse correlations between aliphatic C and log K_{oc} presented by Chin et al. (10), Gauthier et al. (9), and Perminova et al. (32). As a result, these researchers emphasized the strong influence of the aromaticity of NOM on nonionic compounds sorption. We suggest that the poor relationship observed in our study for the whole set of samples indicates that both moieties play an important role in the sorption of pyrene (and possibly other PAHs) to NOM.

The data reported in this study highlight the significance of the aliphatic C-containing groups as a fraction that is at least as important as aromatic structures in binding of pyrene

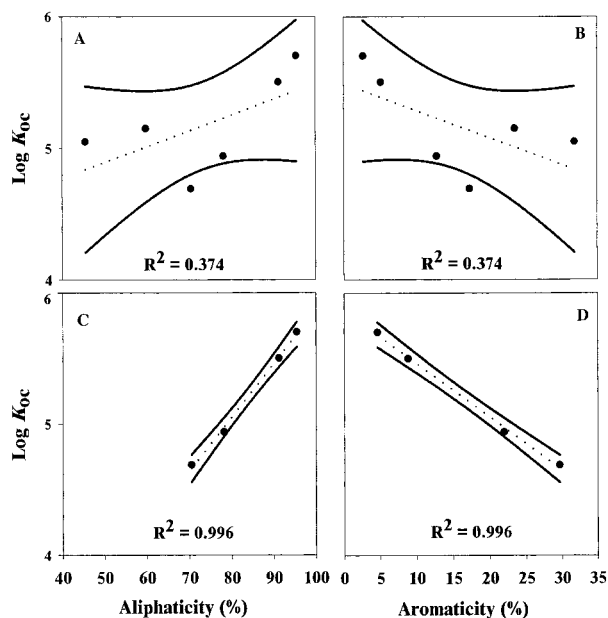


FIGURE 4. Correlations between the pyrene log K_{oc} and the OM aliphaticity (a) and aromaticity (b). Correlations between the pyrene log K_{oc} and the aliphaticity of the OM samples without the degraded lignin and lignite data (c) and aromaticity (d).

and possibly other PAHs. Cuticle and humins samples, which are composed of predominately aliphatic C, exhibited the highest pyrene K_{oc} values. However, the aliphatic structures do not act alone in pyrene sorption. The degraded lignin sample, which has very little paraffinic C-containing groups, also exhibited high pyrene K_{oc} values. Thus, we conclude that various C-containing functional groups are responsible for the sorption of pyrene on NOM surfaces in aqueous systems and that the sorption mechanism is more complex than often perceived.

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