Phenanthrene Sorption to Structurally Modified Humic Acids

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ABSTRACT

Several studies emphasize the importance of soil organic matter characteristics in hydrophobic contaminant sorption and outline the strong dependence of sorption on organic matter aromaticity. In this study, the role of organic matter aromaticity in phenanthrene sorption was investigated using humic acids (HAs) from compost, peat, and soil that were structurally modified by bleaching, hydrolysis, oximation, and subcritical water extraction. The HAs were characterized with cross polarization magic angle spinning carbon-13 nuclear magnetic resonance (CPMAS ^{13}C NMR) spectroscopy and used in batch equilibrations with phenanthrene. Bleaching substantially reduced the aromaticity of the samples whereas the other treatments increased the relative aromaticity. Phenanthrene sorption increased, even though there was a substantial reduction in sorbent aromaticity with some samples. The HAs that exhibited comparable CPMAS ^{13}C NMR spectra and aromaticity did not behave similarly with respect to phenanthrene sorption. When the sorption data (K_{oc} values) were correlated to sample aromaticity, the correlation coefficients (r^2) did not exceed 0.39. Comparisons with the atomic H to C ratio provided slightly better r^2 values (up to 0.54). This study demonstrates that macroscopic sorbent characteristics could not explain the observed phenanthrene sorption coefficients, aliphatic structural components of HAs can contribute appreciably to phenanthrene sorption, and organic matter physical conformation may regulate access to organic matter structures. Therefore, the use of only macroscopic sorbent properties, such as aromaticity, to predict and rationalize sorption values cannot solely be used to explain the behavior of organic contaminants in soil environments.

A MAIN FATE of nonvolatile, nonionic organic contaminants is sorption to soil or sedimentary organic matter (Schwarzenbach et al., 1993). This association is so resilient that desorption rates are slow and several forms of passive remediation, namely bioremediation, are often limited (Weissenfels et al., 1992; Luthy et al., 1997). Hence, there is a need to resolve the fundamental mechanisms involved in sorption processes so that current remedial strategies can be improved. The progression of understanding contaminant behavior has grown from the realization that sorption is proportional to organic matter content (Karickhoff et al., 1979) and to distinct relationships with sorbent quality (Luthy et al., 1997). It is also suggested that organic contaminant sorption can be predicted based on a compound's partitioning in octanol–water systems (Chiou, 1989). Many other studies indicate that bulk or macroscopic sorbent characteristics, such as polarity or aromaticity, can be correlated to and account for differences in sorption behavior (Garbarini and Lion, 1986; Grathwohl, 1990; Xing et al., 1994a). Grathwohl (1990) reported that sorption of chloro-aliphatic chemicals was inversely proportional to the amount of oxygen in the sorbents and suggested that the degree of weathering, in concert with the amount of organic matter, dictated the extent of sorption. Xing et al. (1994b) also reported that organic carbon–normalized sorption coefficients (K_{oc}) for 1-naphthol could be correlated to the polarity index (O + N/C) of the sorbent. The onset and growing application of cross polarization magic angle spinning carbon-13 nuclear magnetic resonance (CPMAS ^{13}C NMR) to obtain essential information on bulk carbon characteristics is routinely applied in sorption studies. This has facilitated conclusions in several investigations that contaminant K_{oc} values are proportional to the aromatic carbon content of the sorbent (Xing et al., 1994a; Huang and Weber, 1997).

Recent studies have indicated that aromaticity is not a suitable soil organic matter variable, especially when used to predict or explain K_{oc} values (Chefetz et al., 2000; Salloum et al., 2001a, b, 2002), which contradicts the popular belief that sorption coefficients can be predicted from macroscopic soil or sedimentary organic matter properties such as the aromatic carbon content. Chefetz et al. (2000) reported that pyrene sorption to organic matter precursors with varying aromaticity correlated as well as with sample aliphaticity and aromaticity, indicating that the application of macroscopic sorbent characteristics to predict sorption coefficients can be misleading. It was found that cuticular plant material, composed mainly of aliphatic structures, sorbed more pyrene than the highly aromatic samples (lignin and lignite). Boyd et al. (1990) also observed higher K_{oc} values for monoaromatic compounds with cuticular material from corn leaf residues than with soil samples. These reports suggest that aliphatic moieties may participate in sorption more than suggested by popular theories, which endorse that aromatic structures govern in sorption reactions. The objective of this study was to further investigate the role of aromatic and aliphatic functionalities in sorption behavior of polycyclic aromatic hydrocarbons (PAHs) to structurally modified humic acids (HAs). Furthermore, this study investigates the reliability of relationships based exclusively on macroscopic measurements.

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Abbreviations: CPMAS, cross polarization magic angle spinning; HA, humic acid; NMR, nuclear magnetic resonance.

MATERIALS AND METHODS

Isolation, Structural Modifications, and Humic Acid Characterization

Humic acids were extracted from the compost, peat, and soil samples as described in Chefetz et al. (2002). The compost was sampled from mature mushroom compost that was prepared from horse manure–straw bedding, poultry manure, gypsum, and brewer's grains. A detailed analysis of the bulk compost sample is presented in Chen et al. (2000). The peat sample was purchased from the International Humic Substances Society (IHSS). The surface soil sample was obtained from the Ellerslie Research Station, located south of the University of Alberta, Edmonton, Canada. This soil was developed under grassy vegetation and over glacial till and is rich in native organic matter (Salloum et al., 2001b).

Chemical modifications of HAs included bleaching, hydrolysis, oximation, and subcritical water extraction. Hydrolysis was performed with 6 M HCl under reflux for 6 h (Almendros, 1994, 1995). Oximation was performed with 3.75 g hydroxylamine hydrochloride in 5 mL pyridine per gram of HA, and the mixture was refluxed for 24 h (Almendros, 1994, 1995). Samples were bleached with 10 g of sodium chlorite, 10 mL of acetic acid, and 100 mL of deionized water per gram of HA. The mixture was stirred overnight until the reaction ceased. After each treatment (hydrolysis, oximation, and bleaching), the solid residue was separated from the mixture via centrifugation (4000 × g for 15 min), and then dialyzed (Spectra/Por membrane, MWCO 6-8000; Fisher Scientific, Pittsburgh, PA) against deionized water. After dialysis, the HAs were removed from the dialysis tubing and freeze-dried. Subcritical water extraction was performed according to the method described in Johnson et al. (1999). This method results in the extraction of polar structural components found in soil samples and promotes aromatization reactions (Johnson et al., 1999, 2001).

Elemental (C, H, and N) analysis was conducted by Quantitative Technologies (Whitehouse, NJ). The C, H, and N contents along with the atomic ratios of C to N and H to C are listed in Table 1. The CPMAS ^{13}C NMR spectra were acquired on a Bruker (Billerica, MA) Avance 300-MHz NMR spectrometer, equipped with a 4-mm H-X MAS probe, and using the standard ramp-CP pulse program (Cook et al., 1996). The acquisition parameters are as described in Salloum et al. (2002). The spectra were integrated into the following chemical shift regions: aliphatic carbon (0–50 ppm); alcohols, amines, carbohydrates, ethers, methoxyl, and acetal carbon (50–112 ppm); aromatic carbon (112–145 ppm); phenolic carbon (145–163 ppm); and carboxyl and carbonyl carbon (163–215 ppm) (Hatcher et al., 1983). Total aromatic carbon was calculated by summing the aromatic and phenolic carbon chemical shift regions (112–163 ppm) and total aliphatic carbon was calculated by summing the paraffinic and substituted alkyl carbon chemical shift regions (0–112 ppm). Aromaticity is expressed as the ratio of total aromatic carbon to the sum of total aliphatic and aromatic carbon (Hatcher et al., 1983). Conversely, aliphaticity is derived from the ratio of total aliphatic carbon to that of total aliphatic plus aromatic carbon.

Phenanthrene Sorption to Humic Acids

Short-term batch equilibrations with phenanthrene were conducted to obtain distribution coefficient (K_d) values used to calculate K_{oc} values (Karickhoff et al., 1979). An aliquot from a concentrated methanol stock of phenanthrene (>98%, ACROS Chemicals/Fisher Scientific, Pittsburgh, PA) was dissolved in a solution containing 5 mM CaCl$_2$ and 0.05 mM HgCl$_2$ to prevent biological degradation of the sorbate without causing significant influences on HA chemistry (Wolf et al., 1989). Methanol concentrations represented 0.5% of the total solution (v/v) and the solution pH was adjusted to 5 because HAs, which are weak acids, will maintain a solid form at this pH (Salloum et al., 2001a).

Phenanthrene solutions (25 mL) of varying concentration (0.2–0.75 mg/L) were added to HA samples (10–100 mg) previously weighed into 25-mL Corex II (Fisher Scientific) glass centrifuge tubes. Five replicates of each starting concentration were assembled, for a total of 20 tubes per isotherm. The tubes were sealed with Teflon-lined screw caps and then placed on an agitator (150 rpm) for 48 h (preliminary tests indicated that apparent equilibrium was reached before this time) at 25°C. 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. Supernatant phenanthrene concentrations were determined by high pressure liquid chromatography as outlined in Salloum et al. (2002). Phenanthrene uptake to the glass walls of the centrifuge tubes was found to be negligible. Hence, the quantity of uptake was measured by difference in solution concentration before and after sorption to the HAs.

Table 1. Carbon, hydrogen, and nitrogen contents of humic acid samples.

Sample	C	H	N	C to N ratio	H to C ratio	Yield†
		%				%
Compost humic acid						
Untreated	55.9	5.7	4.9	13	1.2	NA‡
Bleached	50.6	6.5	5.4	11	1.5	12
Hydrolyzed	62.2	5.3	2.9	25	1.0	59
Oximated	59.0	5.4	7.5	9.2	1.1	48
Subcritical water extracted	65.4	4.8	3.8	20	0.88	ND§
Peat humic acid						
Untreated	55.2	4.1	3.7	18	0.88	NA
Bleached	56.5	6.5	4.2	16	1.4	8
Hydrolyzed	58.8	3.9	2.5	27	0.79	76
Oximated	57.4	3.7	9.4	7.1	0.76	19
Subcritical water extracted	68.7	4.3	4.4	18	0.75	ND
Soil humic acid						
Untreated	49.1	3.8	4.3	13	0.93	NA
Bleached	34.1	3.2	3.3	12	1.1	22
Hydrolyzed	60.3	3.3	2.6	27	0.67	51
Oximated	56.5	3.2	2.7	24	0.68	59
Subcritical water extracted	56.6	3.3	3.5	19	0.69	ND

† Based on total mass before and after modification.
‡ Not applicable.
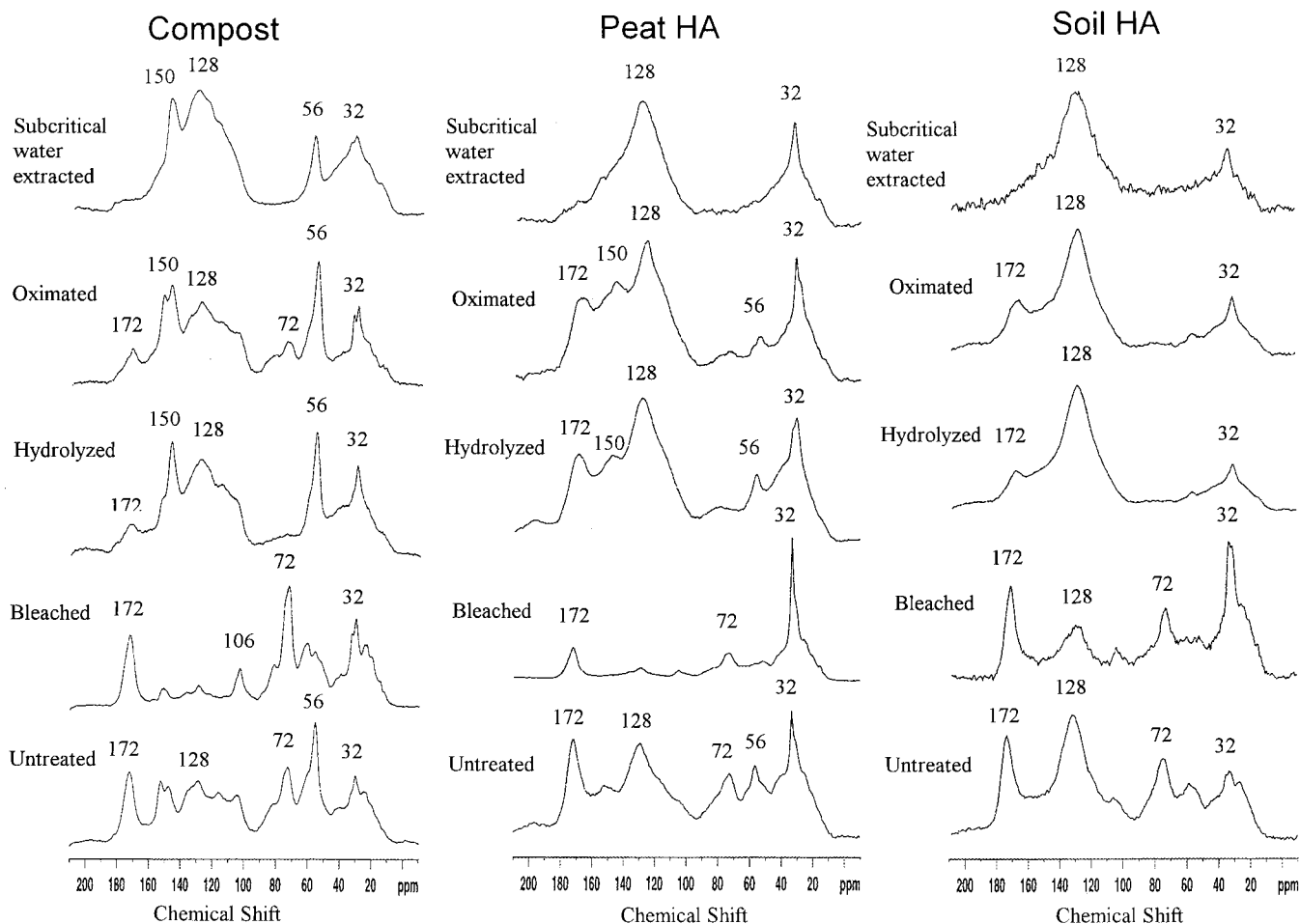§ Not determined due to unrecoverable sample loss during the process.

Fig. 1. Cross polarization magic angle spinning carbon-13 nuclear magnetic resonance (CPMAS ^{13}C NMR) spectra for structurally modified humic acids.

Sorption Coefficients, Isotherms, and Statistical Comparisons

Values for K_d were calculated from the slope of the linear isotherm and the K_{oc} was calculated by dividing K_d by the fraction of organic carbon content in the sample ($K_{oc} = K_d/f_{oc}$) (Karickhoff et al., 1979). Linear regression analysis was performed using Origin Version 6.0 (Microcal Software, 1999) and conducted at a 99% level of confidence. Changes in sorption affinity after HA modification was calculated using ΔK_{oc} (%) = 100% × [(treated HA K_{oc}, mL/g − untreated HA K_{oc}, mL/g)/(untreated HA K_{oc}, mL/g)]. To determine if K_{oc} values significantly increased or decreased after the HA was modified, t tests ($P < 0.01$) were applied to compare the K_{oc} values of modified HAs and those of their corresponding untreated HA (Harris, 1987). Statistical comparisons among treatments were also performed.

RESULTS AND DISCUSSION

Changes in Organic Matter Chemistry due to Structural Modification

The chemical treatments resulted in several specific and nonspecific alterations to the HA structure through the removal, alteration, or enhancement of components in the HA mixture. The CPMAS ^{13}C NMR spectra of the modified HAs and the integration values for the specific chemical shift regions are presented in Fig. 1

and Table 2, respectively. Of the untreated HAs, the soil HA exhibited the highest aromaticity, followed by the peat and compost HA. The chemical modifications were manifested either by an increase or decrease in aromaticity, as well as removal of specific structures.

Bleaching resulted in a substantial reduction of the aromatic carbon signal (128 and 150 ppm) in the CPMAS ^{13}C NMR spectra of all the HA samples. As evident from Fig. 2, the bleached compost and peat HAs are nearly devoid of signals from aromatic carbon. The bleached soil HA still has some residual signal from aromatic carbon (17%) but much less than in the untreated soil HA (29%). The residual aromaticity in the soil HA is probably due to the presence of charcoal because oxidation with sodium hypochlorite (bleaching) cleaves the aromatic rings in organic matter that originate from lignin (Christman et al., 1989). If charcoal or black carbon structures are present, they will resist oxidation. The C to N ratio of the bleached HA samples only decreased slightly from the untreated HA, which implies that C- and N-containing groups were removed nonselectively and that lignin-type carbon may not have been the only structural component that was removed or altered by this treatment. The H to C ratio of the bleached HAs was higher than in their respective un-

Table 2. Cross polarization magic angle spinning carbon-13 nuclear magnetic resonance (CPMAS ^{13}C NMR) integration parameters, aromaticity, and aliphaticity values for humic acids.

Sample	Percentage of C as					Aromaticity	Aliphaticity
	Alkyl C (0–50 ppm)	O-alkyl C (50–112 ppm)	Aromatic C (112–145 ppm)	Aromatic C-O (145–163 ppm)	Carboxyl + carbonyl C (163–215 ppm)		
				%			
Compost humic acid							
Untreated	20	39	22	10	9	34	66
Bleached	31	47	7	3	11	12	88
Hydrolyzed	23	26	33	13	5	48	52
Oximated	18	32	29	15	6	46	54
Subcritical water extracted	23	20	40	14	4	56	44
Peat humic acid							
Untreated	24	28	24	9	15	39	61
Bleached	50	27	8	3	12	12	88
Hydrolyzed	22	21	31	12	15	50	50
Oximated	20	18	34	15	13	56	44
Subcritical water extracted	25	16	42	12	6	57	43
Soil humic acid							
Untreated	17	29	29	9	16	45	55
Bleached	35	30	17	5	13	25	75
Hydrolyzed	16	14	46	12	12	66	34
Oximated	17	13	42	13	15	65	35
Subcritical water extracted	17	21	46	12	4	60	40

treated HAs. This is consistent with the concentration of protonated constituents, such as paraffinic chains, and corresponds to the decline of aromatic carbon and enrichment of aliphatic carbon (32 ppm) as observed in the CPMAS ^{13}C NMR spectra.

Acid hydrolysis has traditionally been used to remove esters, amines, and carbohydrates from humic materials (Parsons, 1989) and to quantify organic matter components (Swift, 1996). The removal of carbohydrates and amines is evident with the decline of signals in the 50 to 112 ppm region of the NMR spectra. Carbohydrate components of organic matter can be identified in NMR spectra by signals at 62 to 66 ppm for C-6 of polysaccharides, 65 to 85 ppm for ring C atoms of polysaccharides, and 105 ppm for the anomeric carbon of polysaccharides (Malcolm, 1989). The removal of the polysaccharides and concentration of the residual components resulted in a relative increase in aromaticity of the HA samples. Acid hydrolysis also resulted in an increase in the atomic C to N ratio for all three HAs (Table 1). This suggests that nitrogen-containing structures, probably peptides, were removed to a greater extent than polysaccharides. The removal of these nonaromatic constituents with acid hydrolysis caused a relative increase in aromaticity (Table 2). The H to C ratios decreased with hydrolysis, indicating that the components remaining after hydrolysis were more condensed (less protonated) than those in the untreated HA.

Oximation resulted in a relative increase of aromatic components in the HA samples. The CPMAS ^{13}C NMR spectra reveal that signals in the carboxyl and carbonyl region as well as the late aliphatic region (70–90 ppm) have decreased. Oximation of humic substances occurs by a reaction of hydroxylamine with carbonyl groups, producing oxime (C=N) groups and a decline in the carbonyl group content (Portal et al., 1986; Leenheer and Noyes, 1989). After oximation, humic substances exhibit more oxime (C=N) and nitro (N–O) constituents (Portal et al., 1986). The transformation of carbonyl groups to oximes should have decreased the

atomic C to N ratio, and this was observed with the compost and peat HAs, but not with the soil HA. The C to N ratio increase of the soil HA implies that N was not incorporated as readily as with the compost and peat HA samples, as has been reported for other soil samples (Almendros, 1994, 1995). The oximation reaction did, however, result in a relative increase in sample aromaticity for all three HAs. The decline in the H to C ratio after oximation and trends in the CPMAS ^{13}C NMR data confirm that protonated constituents of the HA were altered or removed.

Subcritical water extraction resulted in a relative increase of the aromatic carbon signal (128 ppm for the peat and soil HA and 128 and 150 ppm for the compost HA). The high pressure and temperature used in this extraction have been reported to remove polar compounds from whole soil samples while promoting aromatization reactions, and accordingly, increase the relative aromaticity of the sample (Johnson et al., 1999, 2001). From the CPMAS ^{13}C NMR spectra it is evident that the subcritical water removed polar components such as amino acids (α-carbon signal at 60 ppm), carbohydrates (60–85 ppm), aliphatic alcohols (50–55 ppm), as well as carboxylated functionalities (170–175 ppm) because the associated chemical shift signals are no longer apparent after this treatment. Moreover, the increased aromaticity suggests that aromatization reactions with existing components may have occurred during the extraction process. The increase in C to N ratios indicates that subcritical water extraction also removes N-containing organic compounds, such as amino acids, as well as the previously mentioned polar constituents of HAs. The increase in C to N ratios also suggests that this procedure was efficient in removing more N- than C-containing compounds. This observation is in agreement with the decline in H to C ratios that indicates that subcritical water extraction resulted in enrichment in condensed organic matter structures.
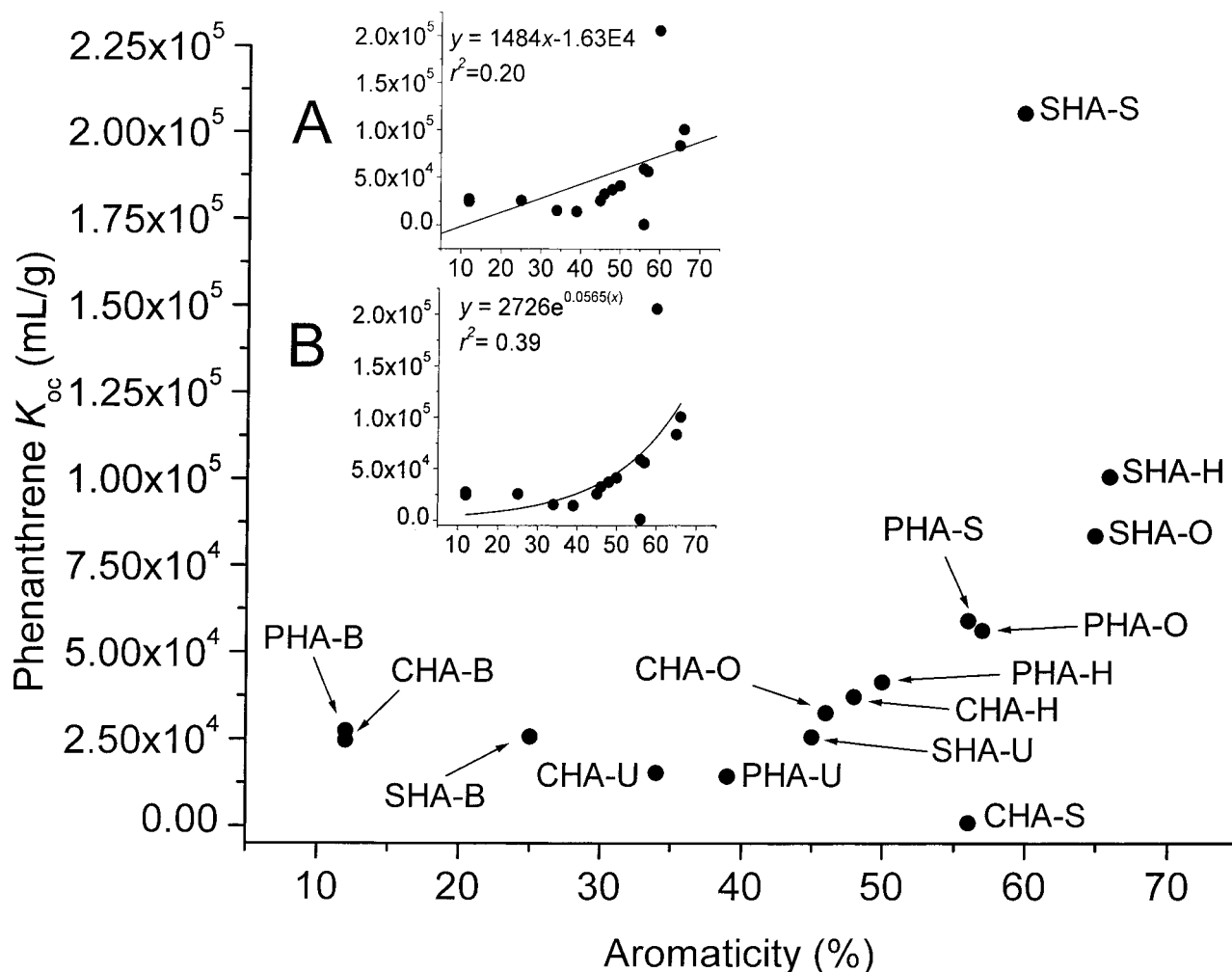
Fig. 2. Comparison of phenanthrene K_{oc} values with humic acid (HA) aromaticity. (*A*) Linear and (*B*) exponential correlations are tested for relationships between K_{oc} values and aromaticity. CHA, compost humic acid; PHA, peat humic acid; SHA, soil humic acid; U, untreated; H, hydrolysis; O, oximated; B, bleached; and S, subcritical water extracted.

Phenanthrene Sorption to Modified Humic Acids

The K_d, K_{oc}, and log K_{oc} values listed in Table 3 are in the range reported for similar sorbents (Laor et al., 1998; Kleineidam et al., 1999; Schultz et al., 1999; Salloum et al., 2002). Among the untreated samples, the soil HA exhibited the highest affinity for phenanthrene. The structural modifications to the HA samples are manifested in the changes of the phenanthrene K_{oc} values (ΔK_{oc}; Table 3). In most instances, the ΔK_{oc} values are positive, representing an increased affinity for phenanthrene after structural modification of the HA. Only two samples (subcritical water extracted compost HA and bleached soil HA) exhibited a decrease in phenanthrene affinity and consequently produced negative ΔK_{oc} values. Statistical comparisons between K_{oc} values before and after chemical treatment indicate that, with the exception of the soil HA, the increase or decrease in sorption is significant before and after bleaching. Comparisons made within the treatment protocols indicted that there are both similarities and differences among the sorbents, implying that the structural changes may have resulted in similar sorption behavior. For ex-

ample, the bleached peat and soil HA have statistically similar K_{oc} values but their CPMAS ^{13}C NMR spectra differ. Conversely, the subcritical water extracted peat and soil HA CPMAS ^{13}C NMR spectra are similar, yet their K_{oc} values statistically differ. These examples indicate that chemically similar sorbents can produce different K_{oc} values and chemically dissimilar sorbents can produce similar K_{oc} values, suggesting that sorbent chemistry alone cannot explain the observed sorption coefficients.

The bleaching treatment, which removed all or a significant portion of the aromatic components produced, increases in phenanthrene sorption with the compost and peat HAs. The K_{oc} of the soil HA did not change after the sample was chemically oxidized even though the aromatic C content declined from 29 to 17%. The bleaching treatment increased sample aliphaticity to 88% in both the compost and peat HAs and their ΔK_{oc} values increased by 64 and 98%, respectively. Bleaching the soil HA also increased the aliphaticity to 75% but this did not significantly result in a change in the observed K_{oc} value. Despite the diminution in aromaticity,

Table 3. Phenanthrene sorption coefficients.†

Sample	K_d	Linear r^2	K_{oc}	Log K_{oc}	ΔK_{oc}‡
	mL/g		mL/g		%
Compost humic acid					
Untreated	8.46×10^3	0.99	1.51×10^4 a§	4.18	
Bleached	1.22×10^4	0.99	$2.41 \times 10^{4**}$ a	4.38	64
Hydrolyzed	2.38×10^4	0.99	$3.83 \times 10^{4**}$ a	4.58	150
Oximated	1.96×10^4	0.98	$3.32 \times 10^{4**}$ a	4.52	120
Subcritical water extracted	6.03×10^2	0.98	$9.23 \times 10^{2**}$ a	2.97	−94
Peat humic acid					
Untreated	7.82×10^3	0.99	1.42×10^4 a	4.15	
Bleached	1.59×10^4	0.99	$2.81 \times 10^{4**}$ b	4.45	98
Hydrolyzed	2.49×10^4	0.99	$4.23 \times 10^{4**}$ b	4.63	200
Oximated	3.28×10^4	0.98	$5.71 \times 10^{4**}$ b	4.76	300
Subcritical water extracted	3.67×10^4	0.98	$5.34 \times 10^{4**}$ b	4.73	280
Soil humic acid					
Untreated	1.32×10^4	0.99	2.69×10^4 b	4.43	
Bleached	8.61×10^3	0.99	2.52×10^4 b	4.40	−6.3
Hydrolyzed	6.10×10^4	0.98	$1.01 \times 10^{5**}$ c	5.00	280
Oximated	4.71×10^4	0.98	$8.34 \times 10^{4**}$ c	4.92	210
Subcritical water extracted	1.02×10^5	0.97	$1.80 \times 10^{5**}$ c	5.26	570

** Significant at the 0.01 probability level when K_{oc} is compared with K_{oc} of the untreated sample.
† K_d, distribution coefficient; K_{oc}, organic carbon–normalized sorption coefficient.
‡ $\Delta K_{oc} = 100\% \times$ [(treated HA K_{oc}, mL/g − untreated HA K_{oc}, mL/g)/(untreated HA K_{oc}, mL/g)], where HA is humic acid.
§ Different letters (a, b, or c) represent a significant difference ($P < 0.01$) when compared with samples within treatment groupings (i.e., comparisons between bleached samples, hydrolyzed samples, etc.).

all three sorbents demonstrate the capability of the aliphatic components to sorb phenanthrene, and this is consistent with the report of the high sorptive affinity of pyrene to a common aliphatic plant biopolymer (plant cuticle; Chefetz et al., 2000). Furthermore, with the compost and peat HA samples, the affinity for phenanthrene surpassed that of the untreated sample, despite the removal of the majority of aromatic components, and is reflected by positive ΔK_{oc} values.

Both the hydrolysis and oximation treatments produced a relative increase in aromaticity in all three HA samples. Subsequent sorption experiments resulted in an escalated affinity for phenanthrene with all the samples subjected to these two treatments. The ΔK_{oc} values increased as much as 300% with oximation and 280% with hydrolysis. The increase in phenanthrene sorption did not conform to any trend within each group of HA samples. For example, the hydrolyzed compost HA sorbed more phenanthrene than the oximated compost HA. This was also observed with the soil HA as the ΔK_{oc} increased from 210% with oximation to 280% with hydrolysis. Alternatively, the ΔK_{oc} of the oximated peat HA (300%) is considerably greater than that for the hydrolyzed peat HA (200%). The CPMAS ^{13}C NMR spectra of the oximated and hydrolyzed spectra reveal only moderate overall structural differences and similar aromatic carbon character, yet the sorption behavior of phenanthrene differs with each treatment, as well as each HA sample. The NMR data indicate that the hydrolysis and oximation procedures caused similar overall changes or removed or modified components that resulted in a comparable generic HA structure. These data demonstrate that chemically similar HAs can differ in phenanthrene sorption, and indicate that phenanthrene sorption may not be governed exclusively by sorbent chemistry. This observation is corroborated by literature reports that conclude that sorbent chemistry could not attribute for the observed differences in K_{oc} values (Salloum et al., 2001a, b; Murphy et al. 1990; Jones

and Tiller, 1999) leading to the hypothesis of another variable in sorption mechanisms, namely organic matter physical conformation.

Phenanthrene sorption to the subcritical water extracted HAs decreased for the compost HA but increased significantly with peat and soil HAs. The phenanthrene K_{oc} for the soil HA increased by almost an order of magnitude after subcritical water extraction. The increase in K_{oc} values for the peat HA (280%) was not as large as with oximation (300%). Nonetheless, the increase in aromaticity and extraction of polar components was favorable with respect to phenanthrene sorption. In contrast, the CPMAS ^{13}C NMR spectrum of the subcritical water extracted compost HA displayed a marked increase in the aromatic carbon signal (128 and 150 ppm) and the calculated aromaticity for this sample is 56%, the highest of all the treatments for the compost HA. However, the ΔK_{oc} is negative (−94%) describing a declined affinity for phenanthrene. A comparison of the subcritical water extracted compost HA CPMAS ^{13}C NMR spectrum with that of the peat and soil HA indicates some differences that may be attributable to the observed differences in sorptive behavior. After subcritical water extraction, both the peat and soil HA spectra display two broad signals (32 and 128 ppm) and are similar to those found in diagenetically altered samples such as subbituminous coals. Furthermore, the signal at 128 ppm can be attributed to highly condensed, aromatic carbon such as that from soot or charcoal. In addition to the signals at 32 and 128 ppm, the compost HA spectrum has peaks that correspond to methoxyl C (56 ppm) and phenolic C (150 ppm) that are characteristic of lignin-derived structures and more polar components. Hence, the difference in sorptive behavior may be due to the distinct types of aromatic structures present. For instance, it has been reported that soot and charcoal structures can dramatically increase K_{oc} values (Bucheli and Gustafsson, 2000). Sorption to lignin has also been reported but the K_{oc} values
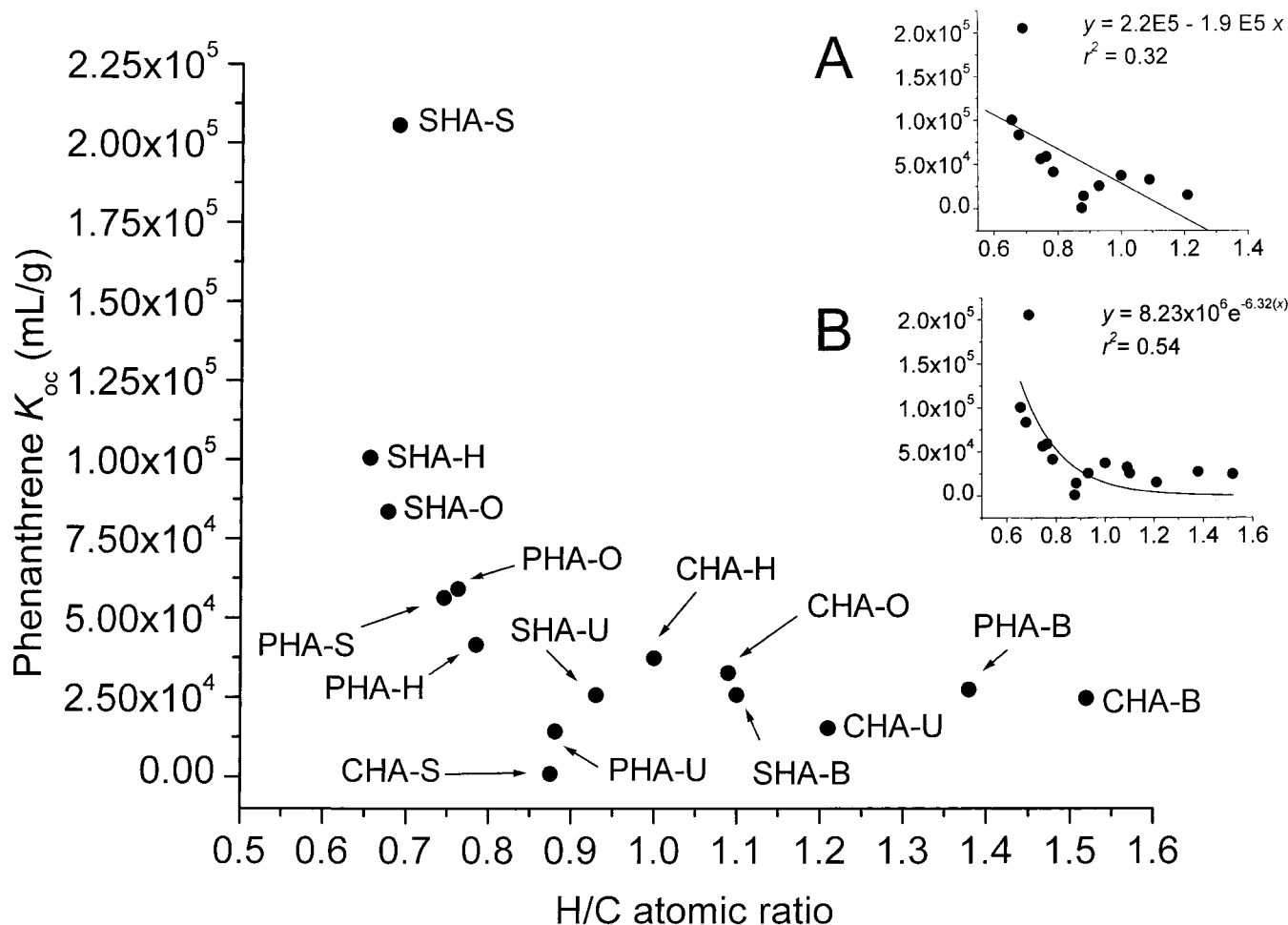
Fig. 3. Comparison of phenanthrene K_{oc} values with the degree of humic acid (HA) condensation (H to C ratio). (A) Linear and (B) exponential correlations are tested for relationships between K_{oc} values and H to C ratios. CHA, compost humic acid; PHA, peat humic acid; SHA, soil humic acid; U, untreated; H, hydrolysis; O, oximated; B, bleached; and S, subcritical water extracted.

are not as high as with more condensed aromatic components (Xing et al., 1994a; Chefetz et al., 2000). Despite this, the large decline in phenanthrene sorption ($\Delta K_{oc} = -94\%$) after subcritical water extraction suggests that the compost HA structure may have undergone substantial physical alteration in conjunction with the increased aromaticity. Thus, to attribute sorption to generic sorbent characteristics may not be appropriate since different types of aromatic carbon, for instance, lignin versus charcoal, can produce significant variations in K_{oc} values. Furthermore, chemical methods routinely employed do not differentiate among aromatic carbon moieties and are unable to detect changes in organic matter physical conformation.

An overall comparison of phenanthrene K_{oc} values with the HA aromaticity is displayed in Fig. 2. It is apparent that a general trend between K_{oc} values and aromaticity exists because most modifications that resulted in an increase of sample aromaticity also produced an increase in the K_{oc} value, noting that some of the samples did not conform to this overall trend. Some literature accounts have reported excellent correlations, in the form of linear or exponential relationships, between organic matter chemistry and sorption values

(Xing et al., 1994a, c; Chefetz et al., 2000; Perminova et al., 1999). Consequently, the data presented here are treated in the same manner. Figures 2A and 2B display linear and exponential model fits, respectively. Both models produced low correlation coefficients (r^2 of 0.20 for the linear model and 0.39 for the exponential model). When the bleached samples were removed from the data set, the linear fit improved; however, the r^2 value only increased to 0.38. In conjunction with aromaticity derived from CPMAS ^{13}C NMR, the degree of condensation interpreted from the atomic H to C ratio has also been used to link organic matter structure with K_{oc} values (Grathwohl, 1990; Salloum et al., 2001b). The phenanthrene K_{oc} values are plotted against the H to C ratio in Fig. 3. As with the comparison against aromaticity, there is a tendency for K_{oc} values to increase as the degree of protonation decreases, but this relationship is ill defined. When attempts are made to correlate the K_{oc} values with the H to C ratios using linear and exponential equations, correlation coefficients of 0.32 and 0.54 are obtained, respectively (Fig. 3A,B).

The modifications made to the HAs resulted in several specific and nonspecific variations to the structure and consequently, many differences in phenanthrene

sorption behavior were observed. Overall, enrichments of aromatic carbon did produce increased phenanthrene K_{oc} values. However, the removal of aromatic structures by bleaching did not produce the decline in phenanthrene sorption one would expect if there was a strict, positive correlation between sorption and sample aromaticity. The observations with the bleached HAs contradict the popular notion that only aromatic structures contribute to hydrophobic compound sorption because a decline in phenanthrene sorption should occur with the removal of aromatic structures. More importantly, the ΔK_{oc} values were positive for the compost and peat HA despite the fact that their relative aromatic carbon content had been significantly reduced. The ability of predominantly aliphatic components of humic materials to sorb hydrophobic compounds has been previously demonstrated with pyrene (Chefetz et al., 2000) and single ring aromatic compounds (Boyd et al., 1990), and is consistent with the observations reported here. Recently, Hu et al. (2000) reported that these aliphatic structures, which are a recalcitrant component of organic matter, have specific chemical characteristics (amorphous and crystalline) that may explain the high affinity of phenanthrene for these aliphatic components. A recent study by Gunasekara et al. (2003) that employed ^1H T_2 relaxation measurements to examine the domain distribution of these humic acids found that the humic acid became more "expanded" after the removal of the aromatic moieties, and explains the increase in phenanthrene sorption values observed in this study.

The remaining alterations (hydrolysis, oximation, and subcritical water extraction) brought about an increase in aromaticity and produced positive ΔK_{oc} values. The enhancement of aromatic carbon did result in an unspecified trend with the corresponding K_{oc} values, noting that this correlation had low correlation coefficients. The difference in the ΔK_{oc} between the hydrolyzed and oximated peat HA samples (200 and 300%, respectively) cannot be explained by aromaticity alone because these samples contain similar amounts of aromatic carbon (50 and 56% aromaticity, respectively). The highest K_{oc} within each group of HAs was associated with a different treatment. For instance, the highest ΔK_{oc} value resulted after hydrolysis for the compost HA, oximation for the peat HA, and subcritical water extraction for the soil HA. The treatments did not generate the same sorption trends within each group of HAs, despite the fact that each alteration modified the HA chemical structure in a similar manner. This may be due to differences in the HA samples themselves, different stages of humification represented by each sample, and nonuniform changes in organic matter physical conformation invoked by the chemical modifications.

The inability for the generic sorbent data to explain the sorption coefficients of contaminants is consistent with other reports that suggest that organic matter physical conformation as well as organic matter chemistry governs the extent of contaminant sorption (Salloum et al., 2001a, b; Murphy et al., 1990; Jones and Tiller, 1999). Furthermore, this study demonstrates that bulk sorbent characteristics obtained from elemental analysis and solid-state NMR cannot be used to predict K_{oc} values. The chemical modifications changed the overall structure and physical conformation of the HAs, therefore limiting or enhancing accessibility of specific structures for phenanthrene sorption. Moreover, the observed capacity for aliphatic constituents to sorb appreciable amounts of phenanthrene further undermines the reliance on aromaticity or other types of macroscopic data to describe and explain sorption of contaminants in soil and sedimentary environments. The extent of the molecular-level structural HA changes is unclear; however, it is certain that bulk chemical data such as aromaticity are insufficient for describing contaminant sorption. Finally, organic matter aliphatic components and organic matter physical conformation deserve more attention in sorption studies, as they appear to play important roles in the sorption and persistence of contaminants in the environment.

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