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Relative Role of Aliphatic and Aromatic Moieties as Sorption Domains for Organic Compounds: A Review

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The sorption behavior of hydrophobic organic compounds (HOCs) in the environment has been the focus of numerous studies. In most of them, the role of aliphatic domains in sorption has been ignored, even although aliphatic components make up a significant portion of the soil organic matter (SOM). The objective of this review is to elucidate the role of the molecular descriptors — aromaticity and aliphaticity — of natural and engineered sorbents as sorption domains for HOCs in the environment. The data, collected from a large and diverse literature data set, show that phenanthrene, like other HOCs, has a strong affinity for aliphatic SOM domains. In many cases, sorption coefficients are higher than those with aromatic-rich sorbents. No significant correlations between either aromaticity or aliphaticity and sorption affinity were recorded for such a large and diverse data set. On the basis of the data set from our literature review of natural and engineered sorbents, we conclude that (*i*) aliphatic structures must be considered in the evaluation of HOC-sorption processes in the environment; (*ii*) neither aromaticity nor aliphaticity of SOM alone can be used to predict the sorption affinity of sorbents having wide and diverse properties; and (*iii*) these molecular descriptors are valuable for relatively homogeneous and chemically similar sorbents.

Introduction

Sorption (adsorption, absorption) is a process by which organic compounds become associated with solid soil and sediment materials. Sorption is highly important because it can significantly affect the fate and behavior of organic chemicals in the environment. The effects of sorption on the fate of these organic compounds are complicated and depend on many factors related to the physicochemical properties of the sorbents and sorbed molecule and on environmental conditions. It is widely accepted that sorption limits the biodegradation of pesticides and other organic contaminants by decreasing their aqueous concentration and limiting their accessibility to enzymes and microorganisms (*1*−*7*). However, some reports have shown that sorption can also enhance biodegradation. For example, Park et al. (*8*) reported that sorption enhances mineralization rates of atrazine and Schnurer et al. (*9*) reported that sorbed glyphosate is microbially degradable. Van Loosdrecht et al. (*10*) suggested that sorption can increase biodegradation by decreasing the toxicity of the substrate to the microorganisms responsible for its degradation. Sorption is also highly important in regulating HOC mobility and transport in the environment. In general, a negative correlation between sorption and mobility has been reported (*11, 12*). However, sorption of HOCs to colloidal materials or to dissolved organic matter can enhance their mobility in the environment due to colloid-facilitated transport (*13*).

Strong dipole interactions between mineral surfaces, such as aluminosilicates and water molecules, decrease the potential sorption of HOCs to minerals and increase the sorption of HOCs by the soil and sedimentary organic matter (SOM). Therefore, the predominant sorbent of HOCs in soils and sediments is the SOM, as long as the total organic carbon is >0.1% (*14*). Because of the high affinity of HOCs to SOM, sorption of HOCs is expressed by an organic carbon normalized sorption coefficient (K_{OC}) rather than on a total sorbent mass basis sorption coefficient (K_d). Gerstel (*15*) reported that values of K_d may vary by several orders of magnitude and the use of K_{OC} greatly reduces this variability. However, the physicochemical nature of the SOM has been suggested as a major factor controlling sorption of organic compounds to soils and sediments (*16*−*21*).

SOM is heterogeneous in composition; in addition its physicochemical nature of SOM can vary greatly as a function of the origin, age, weathering, maturation, and soil depth (*22*−*26*). As a result, SOM cannot be considered as a homogeneous sorption domain for HOCs. For example, Kile et al. (*21*) reported that the K_{OC} values of tetrachloride and 1,2-dichlorobenzene by sediments were about twice those by soils. Xing (*27*) reported that the naphthalene K_{OC} values varied inversely with polarity and directly with aromaticity. Similar results were reported by Grathwohl (*28*) that suggested that an empirical relationship exists between K_{OC} values and the composition of SOM.

The objective of this review is to elucidate the role of the molecular descriptors, namely, aromaticity and aliphaticity as sorption domains for HOCs by an analysis of a large, literature available, diverse data set covering natural and engineered sorbents with vastly different properties. A positive correlation between sorption affinity and aromatic C content of sorbents has been observed in many studies (*18, 29*−*32*). However, a greater sorption affinity of HOCs with aliphatic-rich sorbents has been reported by others (*33*−*36*). This uncertainty may be attributed to the different origin of the sorbents and sample preparation. In many studies, the aromaticity and aliphaticity of the sorbents have either varied within a relatively narrow range or exhibited a wide range of values but for a narrow number of samples that have been chemically or physically modified. This limits

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the generalization of the predominant molecular descriptor, which regulates sorption.

Aromaticity of SOM and Sorption of HOCs. SOM consists mainly of plant residues (e.g., cellular polysaccharides, lignin, proteins, and cuticular materials), materials derived from them via decomposition processes, microbial tissues, and humic substances (*23, 25*). With humification, plant residues are transformed via chemical, biological, and physical processes into more stable forms (humus). During humification, the amount of aromatic and paraffinic carbons increases, whereas the level of O-alkyl carbons decreases (*37*). Therefore, humification and degradation processes result in the loss of some of the characteristic signals of structurally identifiable materials such as polysaccharides and in the enhancement of signals from refractory structures, such as aromatic and alkyl compounds. On a geological scale, diagenesis of organic matter results in the formation of condensed coal-like solids with a low content of oxygen-containing functional groups and a high content of aromatic moieties (*38*).

In view of the dominant level of aromatic moieties in matured organic materials, relationships between sorption affinities of HOCs (mainly polycyclic aromatic hydrocarbons, PAHs) and the level of aromatic carbon in the sorbent have been extensively studied (*24, 29−32, 39−41*). The relative importance of the aromatic moieties of organic sorbents in the sorption of HOCs and the strong positive correlations between sorption affinities and aromaticity are highlighted in those studies. Therefore, the common hypothesis is that an increase in the aromaticity of a sorbent results in an increase in the sorption of nonionic organic contaminants. For example, Chin et al. (*18*) and Perminova et al. (*31*) reported a strong correlation between binding coefficients of PAHs and the molecular weights and aromaticity of humic substances. It was suggested that the aromatic content of the humic substrates significantly influences the binding of aromatic molecules in the environment. Johnson et al. (*30*) used subcritical superheated water treatment to remove polar organic functionalities and to increase the relative level of aromatic carbon residues in soil. They reported that this diagenesis-like process significantly increases the sorption affinity for phenanthrene. Xing (*27*) used a set of soil samples that varied in age, level of diagenesis, and amount of organic matter to examine the influence of sorbent aromaticity on naphthalene sorption. In that study, naphthalene exhibited a higher affinity to mature SOM (originated from shale), rich in aromatic carbon (56%), than that of young SOM (sampled from a surface soil) with low aromatic carbon content (23%). More recently, Tang and Weber (*32*) used superheated water extraction to evaluate the effects of peat alteration on phenanthrene sorption capabilities. As shown in Figure 1, a positive correlation between K_{OC} values of phenanthrene and sorbent aromaticity was obtained (linear correlation coefficient $r^2 = 0.957$). Similar results were also obtained with treated oak leaf and soybean stalk samples (*32*). On the basis of their data, the authors concluded that the sorption−desorption properties of natural organic matter are related to their degree of aromatization and condensation.

The higher sorption of aromatic pollutants to aromatic rather than aliphatic components of natural organic matter was suggested to occur in accordance with their higher solubility in aromatic solvents, such as benzene, versus aliphatic solvents, such as *n*-hexane (*42*). It was also suggested that the improved partitioning of PAHs in SOM results from the enhanced compatibility of their cohesive energy densities with those of the aromatic components in SOM. Increasing polarizability of the PAH in aromatic-rich humic substances was also proposed as an explanation for the preferential interaction of PAHs with aromatic moieties of SOM (*16, 18*). The higher polarizability of aromatic-rich sorbents such as humic materials can increase the van der Waals interactions between the solute and the sorbate. The formation of charge-transfer complexes ($\pi-\pi$ interactions), where PAHs act as electron donors and the aromatic moieties in SOM act as electron acceptors, was also suggested as a possible mechanism enhancing the sorption of aromatic pollutants by aromatic-rich natural sorbents (*43, 44*).

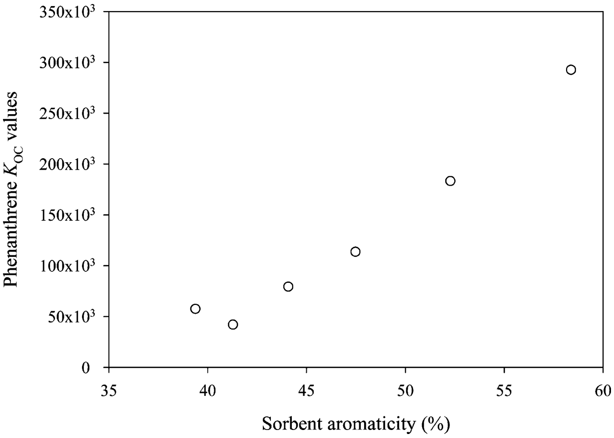

FIGURE 1. Relationship between K_{OC} values of phenanthrene (at an equilibrium concentration of 10 μg/L) and aromaticity of peat samples treated in superheated water for 5 h at different temperatures. Aromaticity was calculated from ^{13}C NMR data by expressing aromatic carbon (100−165 ppm) as a percentage of the aliphatic plus aromatic carbons (0−165 ppm). Modified from Tang and Weber (*32*) and Weber et al. (*92*)

Reports of positive and strong relationships between the sorption affinity of organic pollutants and sorbent aromaticity are not limited to PAHs. For example, Kulikova and Perminova (*41*) reported that, among the tested molecular indices, the strongest relationship ($r^2 = 0.91$) between atrazine K_{OC} values was with the percentage of aromatic carbon (calculated as the 165−187 ppm region in ^{13}C NMR spectra) in humic samples. On the basis of their data, it was concluded that the aromatic core of humic substances provides a better hydrophobic sorption domain for atrazine than the aliphatic structures of the humic substances. However, this mechanism could not predict the observed low atrazine sorption by a sample containing relatively high aromatic contents. Ahmad et al. (*45*) reported a significant positive correlation between SOM aromaticity and K_{OC} values of hydrophobic pesticides. Moreover, they concluded that the aromatic content of SOM can be used as a good predictor of the soil's ability to sorb nonionic pesticides. However, this theory failed to predict high sorption of both pesticides to a soil sample containing highly aliphatic SOM. This latter soil contained a substantial amount of waxy materials, which were suggested to be responsible for its exceptionally high sorption of both pesticides. In another publication, Chiou et al. (*42*) reported that sediments rich in aromatic carbon exhibit higher sorption than soils having low aromatic carbon content but that the differences in aromaticity do not provide a convincing explanation for the differences in observed K_{OC} values between the two data sets.

In this report, we collected a large set of published data on phenanthrene sorption and on the aromaticity and aliphaticity characteristics of sorbents. The relationship between phenanthrene K_{OC} values and the aromaticity level is presented in Figure 2. Unlike the above mentioned positive correlations between K_{OC} values and aromaticity, which were reported for limited and uniform sets of samples (example in Figure 1), no specific correlation between the two parameters is exhibited when a large data set is plotted. It is important to note that the data presented in part A of

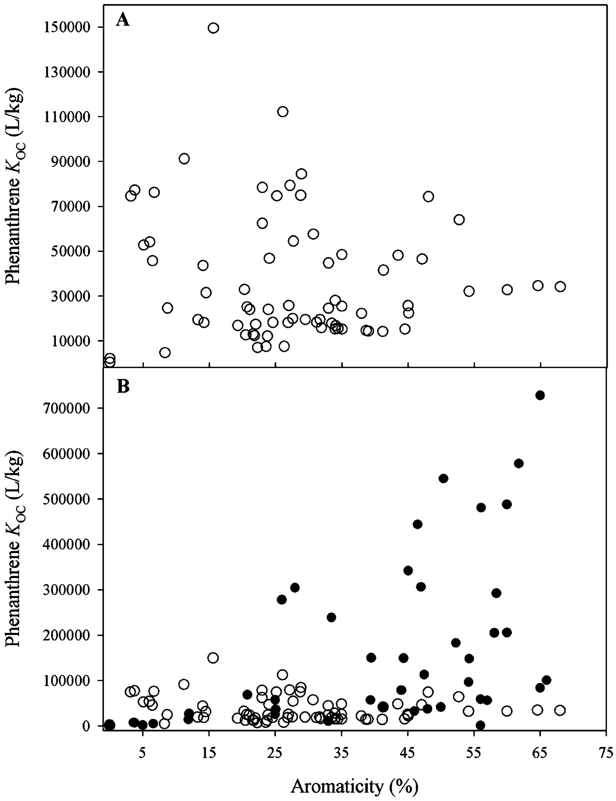

FIGURE 2. Relationship between phenanthrene K_{OC} values (at an equilibrium concentration of 10 μg/L) and the aromaticity level of sorbents: A, data for natural sorbents; B, data for natural (open symbols) and modified (filled symbols) sorbents. Aromaticity was calculated from ^{13}C NMR data by expressing aromatic carbon as percentage of the aliphatic plus aromatic carbons. Data were collected from refs *24, 29, 30, 32, 33, 35, 80, 81, 85, 86, 90–100*.

Figure 2 are only for natural sorbents, including humic substances from different sources, biopolymers (such as cellulose, chitin, lignin, cutin, and cutan), diagenesized samples such as kerogen and humin, and biological samples such as algae, cuticles, and leaves. A larger data set for phenanthrene K_{OC} and aromaticity values is presented in part B of Figure 2 (124 data points). This figure contains, in addition to the data presented in part A of Figure 2, data for chemically or physically modified samples. These modifications include bleaching, acid hydrolysis, charring, and harsh extractions.

In part B of Figure 2, although a significant linear correlation between sorption affinity and aromaticity was not obtained, a general trend of increasing K_{OC} with increasing aromaticity was observed. This trend was due mainly to the modified or engineered samples, as observed in Figure 1. Apparently, when a sample is chemically or physically modified to remove specific functional groups (e.g., polar moieties), a strong correlation between sorption affinity and aromaticity is observed (*30, 32*). However, the data presented in Figure 2 suggest that aromaticity cannot be evaluated as a sole or even major factor influencing the sorption of HOCs in natural samples.

In another report, Chefetz et al. (*34*) studied the sorption of pyrene to SOM fractions with varying aromaticities. They found the sorption affinity of pyrene to a humin sample composed mainly of aliphatic structures (aromaticity value of 8%) was significantly higher than the sorption affinities to highly aromatic samples such as humic acid, lignin, and lignite (aromaticity values of 30, 40, and 55%, respectively). More recently, Lin et al. (*35*) showed a negative correlation between phenanthrene sorption affinities and aromaticity of tea leaf powders. They concluded that aliphatic fractions rather than aromatic moieties regulated the phenanthrene sorption of the tea leaf powders used in their study.

In addition to the positive correlation between sorbent aromaticity and sorption affinity, a positive correlation between sorbent aromaticity and isotherm nonlinearity has been shown in many sorption studies. In general, Freundlich *N* values (used to evaluate sorption linearity) decrease proportionally with increasing aromaticity of the sorbent (*24*). This behavior was explained by assuming that natural and geological organic sorbents consist of at least two types of sorption domains, which can be characterized as expanded and condensed organic structures, analogous to rubbery and glassy synthetic polymers (*46, 47*). Sorption to the rubbery gel-like domain is governed by a solid-phase dissolution (partitioning) process, resulting in reversible, noncompetitive sorption and linear sorption isotherms. However, sorption to the glassy (condensed) domain of SOM is generally nonlinear, exhibiting partially irreversible sorption behavior (desorption hysteresis). The rigid and condensed domains are highly aromatic in nature, having a low content of polar functionalities. Therefore, the dominant interactions between nonpolar sorbates and SOM glassy domains are van der Waals and $\pi-\pi$ interactions. The condensed sorption domains also facilitate hole-filling processes (*48*). Therefore, nonlinear sorption isotherms were exhibited with sorbents rich in rigid or condensed organic domains (*49*). Xing and Pignatello (*48, 50*) concluded that SOM has both partitioning and adsorption domains and that the adsorption sites are internal to the SOM matrix and unevenly distributed with respect to their access to sorbing molecules. Johnson et al. (*30*) and Tang and Weber (*32*) reported that sorption nonlinearity increases with increasing degree of condensation and aromatization and concluded that diagenesis of organic sorbents facilitates an adsorption or hole-filling process that is linked to pore sizes and surfaces. Other studies suggested that black carbon materials, having high surface area and porosity, facilitate nonlinear sorption behavior in soils and sediments (*51–54*). It is important to note that although black carbon materials might contribute significantly to sorption affinity and isotherm nonlinearity, no ideal sorption behavior was also observed by humic materials (*55*).

The data presented in part A of Figure 3 suggest that sorption nonlinearity increases with increasing degree of aromatization (condensation) of natural and modified sorbents. The trend shown in part A of Figure 3 is weaker than the correlations presented for homogeneous sets of samples (*24, 32*). However, the observed negative correlation for this large, diverse data set (124 data points) between sorption nonlinearity and aromaticity further supports the dual-mode sorption model in which sorption to the rubbery state of SOM occurs by dissolution, whereas sorption to the glassy state domain occurs by concurrent dissolution and hole-filling mechanisms (*50*). The data presented in Figure 2 and part A of Figure 3 suggest that the aromatic moieties of SOM sorbents assist nonlinear sorption but not sorption capacity. HOCs are suggested to adsorb to micropores or microvoids present within the aromatic domain. This process is expected to generate nonlinear sorption. Because sorption nonlinearity was not correlated with the aliphatic nature of the samples (part B of Figure 3), we conclude that the nonlinear sorption process is contributed mainly by aromatic moieties of natural sorbents.

Aliphaticity of SOM and Sorption of HOCs. Lorenz at al. (*56*) suggested that refractory SOM fractions are enriched with alkyl-C structures that resist decomposition due to their intrinsic molecular properties. Several other studies have shown that, as decomposition proceeds, aliphatic moieties (rather than or together with aromatic moieties) tend to

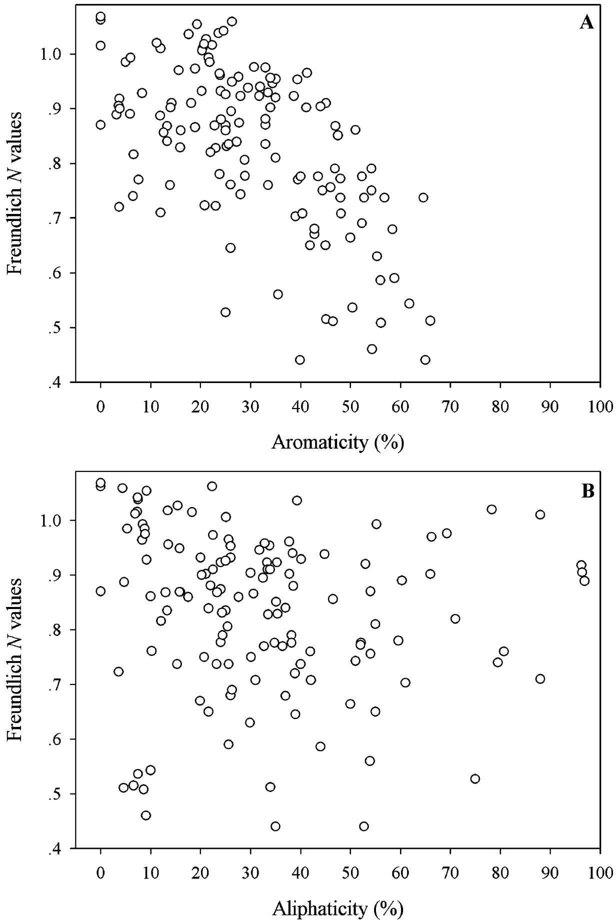

FIGURE 3. Relationship between phenanthrene isotherm nonlinearity (Freundlich *N* value) and aromaticity (A) and aliphaticity (B) of the sorbents. Data were collected from refs *24, 29, 30, 32, 33, 35, 80, 81, 85, 86, 90–100*.

accumulate in soils (*25, 57–60*). Other studies have shown a selective preservation of aliphatic-rich biopolymers with little or no alteration in the environment (*61–65*). The main sources of alkyl-C compounds in soils and terrestrial humic materials are microbial lipids, plant waxes, and above- and below-ground plant biopolymers (*56, 66, 67*). In marine environments, algaenan is the main source of alkyl-C moieties for sedimentary organic matter (*68, 69*).

Chemical degradation methods used to study the properties of SOM and humic materials generally reveal a high proportion of aromatic-type compounds, but the application of ^{13}C NMR spectroscopy has emphasized the importance of aliphatic structures in natural samples. It should be noted that different NMR pulse programs likely have different carbon observability for a given sample. In addition, detection of structural carbons by NMR depends on many factors such as the origin, age, treatment, and processing of the samples and their association with minerals. In this review, we directly take and use the structural carbon distribution data from the literature. These data may not fully represent the actual aliphatic and aromatic C contents. For additional information on NMR methods used to characterize SOM, please refer to Preston (*70, 71*), Dria et al. (*72*), and Cook and Langford (*73*).

The alkyl-C contents vary with SOM fractions and the generic properties of the sample. For example, the alkyl-C content of marine and river sediments, soils, and humic acids has been reported to vary between 20 and 45% (*22, 24, 25, 74–77*). Zech et al. (*25*) reported that humic acids extracted from semiarid soils contain a significantly higher alkyl-C content than humics from forest soils. The high alkyl-C level of natural organic sorbents such as humic acids (isolated from soil and compost), humin (isolated from soil), and kerogen (extracted from sediment) is presented in Figure 4 (^{13}C NMR spectra). The aliphaticity (calculated as the relative level of 0–50 ppm, alkyl-C region, to 0–165 ppm region) and aromaticity (calculated as the relative level of 110–165 ppm region to 0–165 ppm region) values for these samples are respectively 21 and 41% for the soil humic acid, 39 and 24% for the soil humin, 44 and 43% for the kerogen, and 33 and 39% for the compost humic acid. These and other published data (review by Lorenz et al. (*56*)) emphasize the importance of aliphatic structures in natural samples and especially in naturally matured and aged samples such as humin and kerogen.

The vast research in sorption–desorption interactions of HOCs in soils and sediments has largely ignored the sorption potential of an important fraction of many natural sorbents, that is the aliphatic domains. Their contribution to overall uptake is usually considered insignificant. However, Boyd et al. (*78*) reported that corn leaf residues, which are highly aliphatic in nature, exhibit high sorption affinity for HOCs. In the past decade, several studies emphasizing the role of aliphatic moieties of SOM in HOC sorption have been published (*33, 34, 36, 79–81*). Hu et al. (*57*) suggested that humic acids contain a significant fraction of a substance that acts like polyethylene crystallites with ^{13}C NMR peaks at 32.9 and 31.0 ppm. These two peaks correspond respectively to the rigid all-trans and the mobile gauche-containing $(CH_2)_n$ units of a long-chain polyethylene-like polymer. It was suggested that these mobile amorphous regions play a role in the sorption of nonpolar molecules. Similar conclusions were also drawn by Sachleben et al. (*82*), who used 1D and 2D NMR experiments to examine the interactions between pyrene and cuticular materials. Variable-temperature NMR experiments showed that cutan, a polyethylene-like biopolymer, undergoes the characteristic melting behavior of polyethylene-like crystallites and that pyrene is in close proximity to paraffinic moieties after sorption. In another study, Chefetz et al. (*34*) tested the sorption of pyrene to a series of sorbents comprised of different levels of aromaticity and aliphaticity. In that study, a positive trend was observed between the K_{OC} level and the aliphaticity of the set of samples. Similar conclusions were also presented by Kopinke et al. (*79*). They performed sorption experiments with pyrene and a set of different sorbents, among them highly aliphatic synthetic polymers. This study clearly demonstrated that short aliphatic chains are more effective than aromatic moieties in binding pyrene.

A similar trend was also observed with humic substances – higher sorption affinity of PAHs was reported for humin samples than for humic acid samples, even though the aromaticity of the humic acid was much higher than that of the humin (*76*). Additionally, Mao et al. (*83*) observed that the aliphatic carbon fraction, rather than the aromatic one, is strongly correlated to HOC sorption. They showed the sorption of phenanthrene to be strongly correlated with the content of the amorphous nonpolar aliphatic domains. The hydrophobicity and relatively low density of the amorphous poly(methylene) regions are similar to those of alkane solvents, and they were therefore suggested as an ideal environment for the partitioning of HOCs (*84*).

The relationship between phenanthrene K_{OC} values and aliphaticity in a large data set is presented in Figure 5. The data presented in part A of Figure 5 are for natural sorbents not including samples that were chemically or physically altered after they were extracted (this set of data is similar to the data set presented in part A of Figure 2). The data presented in part B of Figure 5, similar to those presented in part B of Figure 2, are for the whole collected data set, including the natural sorbents and the samples that were chemically or physically altered post-extraction. The data

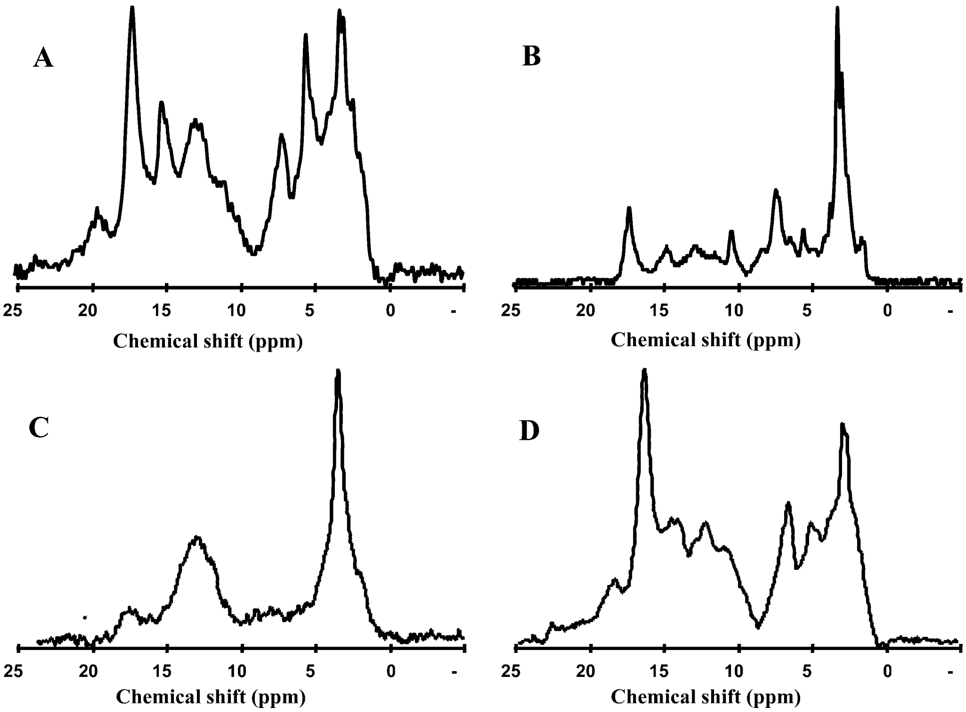

FIGURE 4. ^{13}C NMR spectra of soil humic acid (A), soil humin (B), kerogen from sediment (C), and compost humic acid (D). Modified from Kang and Xing (*90*), Mashayekhi et al. (*80*), and Sun et al. (*36*).

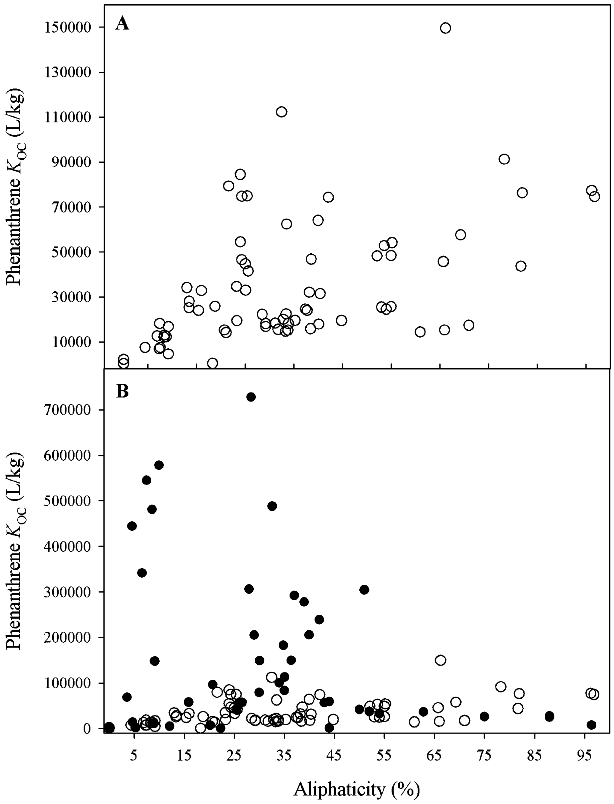

FIGURE 5. Relationship between phenanthrene K_{OC} values (at an equilibrium concentration of 10 μg/L) and aliphaticity of organic sorbents: A, data for natural sorbents; B, data for natural (open symbols) and modified (filled symbols). Aliphaticity was calculated from ^{13}C NMR data by expressing paraffinic carbon (0–50 ppm) as a percentage of the aliphatic plus aromatic carbons (0–165 ppm). Data were collected from refs *24, 29, 30, 32, 33, 35, 80, 81, 85, 86, 90–100.*

for the whole set of samples (part B of Figure 5) exhibited no relationship between binding coefficients and aliphaticity. Moreover, the highest phenanthrene K_{OC} values were obtained for samples having a relatively low level of aliphaticity (<35%). However, when the chemically and physically altered samples were excluded (part A of Figure 5), a general trend of increasing phenanthrene K_{OC} values with increasing aliphaticity was observed. This trend is weaker than the positive correlation between K_{OC} values of PAHs and aliphaticity in small and homogeneous sets of samples, as presented by Chefetz et al. (*34*), Lin et al. (*35*), and Salloum et al. (*85*). This is probably because of the use of a diverse data set covering sorbents with different properties. Within this data set, the relative level of the amorphous- and crystalline-alkyl structures, which exhibit various sorptive capacities, was different. Therefore, it is not surprising that the clear correlation curve often exhibited for small sets of carefully selected samples was not observed here.

Hu et al. (*57*) suggested that nonionic organic contaminants would sorb primarily to the amorphous polymethylene structures in humic materials. Thus, a better correlation is expected between sorption affinity and the level of amorphous domains, rather than the total level of aliphaticity. In accordance with this hypothesis, Salloum et al. (*85*) reported that samples devoid of amorphous paraffinic carbon exhibit the lowest phenanthrene K_{OC} values, whereas sorbents that contain a large amount of amorphous methylene carbon produce high phenanthrene K_{OC} values. For the latter sample, the K_{OC} value was higher than that for aromatic-rich sorbents.

The role of amorphous polymethylene structures as a major sorption domain for HOCs is also supported by the positive correlation between phenanthrene K_{OC} values and the aliphaticity of tea leaves (*35*). In that study, all of the sorbents exhibited a broad peak of 0–30 ppm belonging to amorphous alkyl-C, and no clear rigid alkyl-C peak. Therefore, a strong and positive linear correlation was observed between the two variables. Similar conclusions were also suggested to explain the higher sorption of HOCs to cutin than to cutan, even though the latter biopolymer is characterized by a higher level of alkyl-C (*86, 87*). In those studies, the level of crystalline alkyl-C did not correlate with the sorption and desorption behaviors. It was therefore concluded that the 31.5 ppm peak in the ^{13}C NMR spectra can be assigned to a more condensed and rigid alkyl-C structure, rather than to pure polyethylene-like crystallites, which are expected to be resistant to environmental attack but to contribute only little to sorption.

This hypothesis is supported by the lack of correlation between the linearity of sorption and alkyl-C level. Whereas the amorphous sorption domain promotes linear sorption, the more condensed alkyl-C sorption domain probably facilitates nonlinear sorption (hole-filling-type sorption). Therefore, no correlation between the isotherm linearity and the total level of aliphaticity is expected (part B of Figure 3). Sorbents that contain predominantly amorphous methylene carbon are expected to exhibit linear sorption isotherms (*35*). It was concluded that the mobile amorphous regions of the alkyl-C may play a significant role in the linear sorption (partitioning) of nonpolar molecules in soil. The rigid-type alkyl-C domains of SOM probably promote limited-capacity sorption, similar to the aromatic moieties. Therefore, the relative level of each of the sorption domains will determine the overall sorption affinity of HOC to the alkyl-C domain and the sorption linearity. This dual sorptive behavior of SOM alkyl-C moieties fits with the dual-mode model concept of sorption in which dissolution and hole-filling mechanisms take place concurrently (*50*).

It is important to note that other factors such as accessibility and conformation can also influence the sorption ability of alkyl-C structures (*88, 89*). The alkyl-C structures may not always be accessible for sorption due to interactions with other structural components of SOM. These interactions can physically prevent the sorbate molecule's access to the sorption domain (*33*). Similarly, polarity can also reduce the sorption affinity. For example, Kang and Xing (*90*) suggested that the high K_{OC} values observed for both aromatic- and aliphatic-rich sorbets was due to their low polarity. It was concluded that the polarity of SOM is the predominant regulator for the magnitude of HOC sorption rather than structure properties (e.g., aromaticity or aliphaticity). It is also important to note that a negative relationship between polarity and the level of paraffinic carbon of organic sorbents was reported (*33, 85, 86, 88, 91*). This suggests that polarity and alkyl-C could be interactive parameters regulating sorption of organic pollutants. The polarity data were not available for the whole analyzed data set but analysis of part of the samples (data not presented) exhibited no correlation between polarity and K_{OC} values. This emphasizes that polarity, as aromaticity or aliphaticity, might be used as molecular parameters to evaluate sorption but only for chemically similar sorbents.

Prospects. In the present review, we evaluated the role of aliphatic and aromatic structures of SOM as sorption domains for HOCs. The vast research in sorption−desorption interactions of HOCs in soils and sediments has largely ignored the sorption potential of nonaromatic (i.e., aliphatic) domains, which are considered an important and refractory fraction of SOM. In contrast, many studies emphasize the role of aromatic structures as sorption domains for HOCs, showing strong positive correlations between sorption affinity and aromaticity. However, many of these correlation curves do not pass through the origin. This suggests that alkyl-C moieties, in addition to aromatic moieties, can act as sorption domains for HOCs in natural organic sorbents. On the basis of our review of this large and diverse data set of natural and engineered sorbents, we conclude that alkyl-C moieties can sorb appreciable amounts of HOCs, in some cases with even higher affinity than aromatic-rich sorbents. However, it is important to note that black carbon materials typically exhibit sorptive capabilities higher than humic materials and the aliphatic-rich sorbents reviewed here (*54*).

In general, poor correlations were obtained between the two investigated molecular descriptors (i.e., aromaticity and aliphaticity) and sorption affinity. This suggests that these chemical properties of SOM cannot predict sorption affinity of sorbents having wide and diverse properties. However, aliphaticity and aromaticity can be used to evaluate the sorption properties of sorbents originating from a similar source and/or of a similar nature.

The poor correlation between sorption affinity data and the aromaticity of natural sorbents (part A of Figure 2) and the positive correlation between sorption nonlinearity and aromaticity (part A of Figure 3) suggests that aromatic domains do not necessarily govern the sorption affinity of HOCs; rather, they contribute to the nonlinear or hole-filling type of HOC sorption, probably due to microvoids present within the condensed aromatic domains. The alkyl-C structures of SOM consist of two types of sorption domains: rigid and mobile (*57*). The mobile amorphous domain probably facilitates dissolution (partitioning) and therefore promotes linear and reversible isotherms. The rigid or condensed alkyl-C domain exhibits lower sorptive capacity than the mobile fraction. Therefore, the relative levels of these two sorption domains determine the overall sorption capability of the alkyl-C structure, which needs to be addressed in future investigations.

To better understand the role of alkyl-C structures of SOM as sorption domains, specific structures need to be linked to sorption/desorption behavior. The following research directions may help to achieve this goal: improving determinations of the contact of the rigid and mobile alkyl-C domains, constructing multisite models to link between alkyl-C and aromatic moieties and sorption−desorption behaviors, determining the accessibility of alkyl-C and aromatic domains, defining the relative contribution of polar alkyl- and aromatic-C moieties for the sorption of polar and nonpolar contaminants, characterizing the degradability and transformation of alkyl-C moieties in soils, and determining the associations of alkyl-C moieties and minerals in soils and sediments.

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Literature Cited

(1) Rao, P. S. C.; Bellin, C. A.; Brusseau, M. L. Coupling biodegradation of organic chemicals to sorption and transport in soils and aquifers: Paradigms and paradoxes. In *Sorption and Degradation of Pesticides and Organic Chemicals in Soil*; Linn, D. M., Carski, T. H., Brusseau, M. L., Chang, A. C., Eds.; SSSA and ASA: Madison, WI, 1993; Vol. SSSA Spec. Publ. 32, pp 1−26.

(2) Scow, K. M., Effect of sorption-desorption and diffusion processes on the kinetics of biodegradation of organic chemicals in soil. In *Sorption and Degradation of Pesticides and Organic Chemicals in Soil*; Linn, D. M., Carski, T. H., Brusseau, M. L., Chang, F.-H., Eds.; SSSA and ASA: Madison, WI, 1993; Vol. *SSSA Spec. Publ. 32.*, pp 73−114.

(3) Guthrie-Nichols, E.; Grasham, A.; Kazunga, C.; Sangaiah, R.; Gold, A.; Bortiatynski, J.; Salloum, M.; Hatcher, P. The effect of aging on pyrene transformation in sediments. *Environ. Toxicol. Chem.* **2003**, *22* (1), 40–49.

(4) Guo, L.; Wagenet, R. J.; Jury, W. A. Adsorption effects on kinetics of aldicarb degradation: equilibrium model and application to incubation and transport experiments. *Soil Sci. Soc. Am. J.* **1999**, *63* (6), 1637–1644.

(5) Gamerdinger, A. P.; Achin, R. S.; Traxler, R. W. Approximating the impact of sorption on biodegradation kinetics in soil-water system. *Soil Sci. Soc. Am. J.* **1997**, *61* (6), 1618–1626.

(6) Ogram, A. V.; Jessup, R. E.; Ou, L. T.; Rao, P. S. Effects of sorption on biological degradation rates of (2,4-dichlorophenoxy) acetic acid in soils. *Appl. Environ. Microbiol.* **1985**, *49* (3), 582–587.

(7) Smith, S. C.; Ainsworth, C. C.; Traina, S. J.; Hicks, R. J. Effect of sorption on the biodegradation of quinoline. *Soil Sci. Soc. Am. J.* **1992**, *56* (3), 737–746.

(8) Park, J.-H.; Feng, Y.; Ji, P.; Voice, T. C.; Boyd, S. A. Assessment of bioavailability of soil-sorbed atrazine. *Appl. Environ. Microbiol.* **2003**, *69* (6), 3288–3298.

(9) Schnurer, Y.; Persson, P.; Nilsson, M.; Nordgren, A.; Giesler, R. Effects of surface sorption on microbial degradation of glyphosate. *Environ. Sci. Technol.* **2006**, *40* (13), 4145–4150.

(10) Van Loosdrecht, M. C.; Lyklema, J.; Norde, W.; Zehnder, A. J. Influence of interfaces on microbial activity. *Microbiol. Mol. Biol. Rev.* **1990**, *54* (1), 75–87.

(11) Jury, W. A.; Focht, D. D.; Farmer, W. J. Evaluation of pesticide groundwater pollution potential from standard indices of soil-chemical adsorption and biodegradation. *J. Environ. Qual.* **1987**, *16* (4), 422–428.

(12) Pignatello, J. J.; Ferrandino, F. J.; Huang, L. Q. Elution of aged and freshly added herbicides from a soil. *Environ. Sci. Technol.* **1993**, *27* (8), 1563–1571.

(13) Laegdsmand, M.; de Jonge, L. W.; Moldrup, P.; Keiding, K. Pyrene sorption to water-dispersible colloids: Effect of solution chemistry and organic matter. *Vadose Zone J.* **2004**, *3* (2), 451–461.

(14) Schwarzenbach, R. P.; Westall, J. Transport of nonpolar organic compounds from surface water to groundwater. Laboratory sorption studies. *Environ. Sci. Technol.* **1981**, *15* (11), 1360–1367.

(15) Gerstel, Z. Estimation of organic chemical sorption by soils. *J. Contam. Hydrol.* **1990**, *6*, 357–375.

(16) Gauthier, T. D.; Seitz, W. R.; Grant, C. L. Effects of structural and compositional variations of dissolved humic materials on pyrene *K*oc values. *Environ. Sci. Technol.* **1987**, *21* (3), 243–248.

(17) Luthy, R. G.; Aiken, G. R.; Brusseau, M. L.; Cunningham, S. D.; Gschwend, P. M.; Pignatello, J. J.; Reinhard, M.; Traina, S. J.; Weber, W. J.; Westall, J. C. Sequestration of hydrophobic organic contaminants by geosorbents. *Environ. Sci. Technol.* **1997**, *31* (12), 3341–3347.

(18) Chin, Y. P.; Aiken, G. R.; Danielsen, K. M. Binding of pyrene to aquatic and commercial humic substances: The role of molecular weight and aromaticity. *Environ. Sci. Technol.* **1997**, *31* (6), 1630–1635.

(19) Rutherford, D. W.; Chiou, C. T.; Kile, D. E. Influence of soil organic matter composition on the partition of organic compounds. *Environ. Sci. Technol.* **1992**, *26* (2), 336–340.

(20) Chiou, C. T.; Kile, D. E.; Rutherford, D. W.; Sheng, G.; Boyd, S. A. Sorption of selected organic compounds from water to a peat soil and its humic-acid and humin fractions: Potential sources of the sorption nonlinearity. *Environ. Sci. Technol.* **2000**, *34* (7), 1254–1258.

(21) Kile, D. E.; Wershaw, R. L.; Chiou, C. T. Correlation of soil and sediment organic matter polarity to aqueous sorption of nonionic compounds. *Environ. Sci. Technol.* **1999**, *33* (12), 2053–2056.

(22) Chefetz, B.; Chen, Y.; Clapp, C. E.; Hatcher, P. G. Characterization of organic matter in soils by thermochemolysis using tetramethylammonium hydroxide (TMAH). *Soil Sci. Soc. Am. J.* **2000**, *64* (2), 583–589.

(23) Stevenson, F. J. *Humus Chemistry: Genesis, Composition, Reactions*; John Wiley and Sons: New York, 1994.

(24) Xing, B. Sorption of naphthalene and phenanthrene by soil humic acids. *Environ. Pollut.* **2001**, *111* (2), 303–309.

(25) Zech, W.; Senesi, N.; Guggenberger, G.; Kaiser, K.; Lehmann, J.; Miano, T. M.; Miltner, A.; Schroth, G. Factors controlling humification and mineralization of soil organic matter in the tropics. *Geoderma* **1997**, *79*, 117–161.

(26) Song, J.; Peng, P. a.; Huang, W. Black carbon and kerogen in soils and sediments. 1. Quantification and characterization. *Environ. Sci. Technol.* **2002**, *36* (18), 3960–3967.

(27) Xing, B. The effect of the quality of soil organic matter on sorption of naphthalene. *Chemosphere* **1997**, *35* (3), 633–642.

(28) Grathwohl, P. Influence of organic matter from soils and sediments from various origins on the sorption of some chlorinated aliphatic hydrocarbons: Implications on Koc correlations. *Environ. Sci. Technol.* **1990**, *24* (11), 1687–1693.

(29) Johnson, M. D.; Huang, W.; Weber, W. J., Jr. A distributed reactivity model for sorption by soils and sediments. 13. *Environ. Sci. Technol.* **2001**, *35* (8), 1680–1687.

(30) Johnson, M. D.; Huang, W.; Dang, Z.; Weber, W. J., Jr. A distributed reactivity model for sorption by soils and sediments. 12. *Environ. Sci. Technol.* **1999**, *33* (10), 1657–1663.

(31) Perminova, I. V.; Grechishcheva, N. Y.; Petrosyan, V. S. Relationships between structure and binding affinity of humic substances for polycyclic aromatic hydrocarbons: relevance of molecular descriptors. *Environ. Sci. Technol.* **1999**, *33* (21), 3781–3787.

(32) Tang, J.; Weber, W. J. Development of engineered natural organic sorbents for environmental applications. 2. Sorption characteristics and capacities with respect to phenanthrene. *Environ. Sci. Technol.* **2006**, *40* (5), 1657–1663.

(33) Chefetz, B. Sorption of phenanthrene and atrazine by plant cuticular fractions. *Environ. Toxicol. Chem.* **2003**, *22*, 2492–2498.

(34) Chefetz, B.; Deshmukh, P. A.; Hatcher, P. G.; Guthrie, E. A. Pyrene sorption by natural organic matter. *Environ. Sci. Technol.* **2000**, *34*, 2925–2930.

(35) Lin, D.; Pan, B.; Zhu, L.; Xing, B. Characterization and phenanthrene sorption of tea leaf powders. *J. Agric. Food Chem.* **2007**, *55* (14), 5718–5724.

(36) Sun, K.; Ran, Y.; Yang, Y.; Xing, B. Sorption of phenanthrene by nonhydrolyzable organic matter from different size sediments. *Environ. Sci. Technol.* **2008**, *42* (6), 1961–1966.

(37) Kelleher, B. P.; Simpson, M. J.; Simpson, A. J. Assessing the fate and transformation of plant residues in the terrestrial environment using HR-MAS NMR spectroscopy. *Geochim. Cosmochim. Acta* **2006**, *70* (16), 4080–4094.

(38) Simpson, M. J.; Hatcher, P. G. Determination of black carbon in natural organic matter by chemical oxidation and solid-state 13C nuclear magnetic resonance spectroscopy. *Org. Geochem.* **2004**, *35* (8), 923–935.

(39) Huang, W.; Weber, W. J., Jr. A distributed reactivity model for sorption by soils and sediments. 10. *Environ. Sci. Technol.* **1997**, *31* (9), 2562–2569.

(40) Weber, W. J., Jr.; Huang, W. L. A distributed reactivity model for sorption by soils and sediments. 4. Intraparticle heterogeneity and phase-distribution relationships under nonequilibrium conditions. *Environ. Sci. Technol.* **1996**, *30* (3), 881–888.

(41) Kulikova, N. A.; Perminova, I. V. Binding of atrazine to humic substances from soil, peat, and coal related to their structure. *Environ. Sci. Technol.* **2002**, *36* (17), 3720–3724.

(42) Chiou, C. T.; McGroddy, S. E.; Kile, D. E. Partition characteristics of polycyclic aromatic hydrocarbons on soils and sediments. *Environ. Sci. Technol.* **1998**, *32* (2), 264–269.

(43) Sander, M.; Pignatello, J. J. Characterization of charcoal adsorption sites for aromatic compounds: insights drawn from single-solute and bi-solute competitive experiments. *Environ. Sci. Technol.* **2005**, *39* (6), 1606–1615.

(44) Zhu, D.; Pignatello, J. J. Characterization of aromatic compound sorptive interactions with black carbon (charcoal) assisted by graphite as a model. *Environ. Sci. Technol.* **2005**, *39* (7), 2033–2041.

(45) Ahmad, R.; Kookana, R. S.; Alston, A. M.; Skjemstad, J. O. The nature of soil organic matter affects sorption of pesticides. 1. Relationships with carbon chemistry as determined by ^{13}C CPMAS NMR spectroscopy. *Environ. Sci. Technol.* **2001**, *35* (5), 878–884.

(46) Ju, D. Y.; Young, T. M. The influence of natural organic matter rigidity on the sorption, desorption, and competitive displacement rates of 1,2-dichlorobenzene. *Environ. Sci. Technol.* **2005**, *39* (20), 7956–7963.

(47) Weber, W. J., Jr.; Huang, W.; Yu, H. Hysteresis in the sorption and desorption of hydrophobic organic contaminants by soils and sediment: 2. Effects of soil organic matter heterogeneity. *J. Contam. Hydrol.* **1998**, *31*, 149–165.

(48) Xing, B. S.; Pignatello, J. J. Time-dependent isotherm shape of organic compounds in soil organic matter: implications for sorption mechanism. *Environ. Toxicol. Chem.* **1996**, *15* (8), 1282–1288.

(49) Ran, Y.; Huang, W.; Rao, P. S. C.; Liu, D.; Sheng, G.; Fu, J. The role of condensed organic matter in the nonlinear sorption of hydrophobic organic contaminants by a peat and sediments. *J. Environ. Qual.* **2002**, *31* (6), 1953–1962.

(50) Xing, B.; Pignatello, J. J. Dual-mode sorption of low-polarity compounds in glassy poly(vinyl chloride) and soil organic matter. *Environ. Sci. Technol.* **1997**, *31* (3), 792–799.

(51) Cornelissen, G.; Gustafsson, O. Importance of unburned coal carbon, black carbon, and amorphous organic carbon to phenanthrene sorption in sediments. *Environ. Sci. Technol.* **2005**, *39* (3), 764–769.

(52) Cornelissen, G.; Gustafsson, O. Sorption of phenanthrene to environmental black carbon in sediment with and without organic matter and native sorbates. *Environ. Sci. Technol.* **2004**, *38* (1), 148–155.

(53) Cornelissen, G.; Breedveld, G. D.; Kalaitzidis, S.; Christanis, K.; Kibsgaard, A.; Oen, A. M. P. Strong sorption of native PAHs to pyrogenic and unburned carbonaceous geosorbents in sediments. *Environ. Sci. Technol.* **2006**, *40* (4), 1197–1203.

(54) Koelmans, A. A.; Jonker, M. T. O.; Cornelissen, G.; Bucheli, T. D.; Van Noort, P. C. M.; Gustafsson, O. Black carbon: The reverse of its dark side. *Chemosphere* **2006**, *63* (3), 365–377.

(55) Pignatello, J. J.; Lu, Y. F.; LeBoeuf, E. J.; Huang, W. L.; Song, J.; Xing, B. S. Nonlinear and competitive sorption of apolar compounds in black carbon-free natural organic materials. *J. Environ. Qual.* **2006**, *35* (4), 1049–1059.

(56) Lorenz, K.; Lal, R.; Preston, C. M.; Nierop, K. G. J. Strengthening the soil organic carbon pool by increasing contributions from recalcitrant aliphatic bio(macro)molecules. *Geoderma* **2007**, *142* (1−2), 1–10.

(57) Hu, W.; Mao, J.; Xing, B.; Schmidt-Rohr, K. Poly(methylene) crystallites in humic substances detected by nuclear magnetic resonance. *Environ. Sci. Technol.* **2000**, *34* (3), 530–534.

(58) Stimler, K.; Xing, B.; Chefetz, B. Transformation of plant cuticles in soil: Effect on their sorptive capabilities. *Soil Sci. Soc. Am. J.* **2006**, *70* (4), 1101–1109.

(59) Baldock, J. A.; Oades, J. M.; Nelson, P. N.; Skene, T. M.; Golchin, A.; Clarke, P. Assessing the extent of decomposition of natural organic materials using solid-state ^{13}C NMR spectroscopy. *Aust. J. Soil Res.* **1997**, *35*, 1061–1083.

(60) Chefetz, B.; Tarchitzky, J.; Deshmukh, A. P.; Hatcher, P. G.; Chen, Y. Structural characterization of humic substances in particle-size fraction of an agricultural soil. *Soil Sci. Soc. Am. J.* **2002**, *66*, 129–141.

(61) Almendros, G.; Dorado, J.; Gonzales-Vila, F. J.; Blanco, M. J.; Lankes, U. ^{13}C NMR assessment of decomposition patterns during composting of forest and shrub biomass. *Soil Biol. Biochem.* **2000**, *32*, 739–804.

(62) Almendros, G.; Guadalix, M. E.; Gonzalez-Vila, F. J.; Martin, F. Preservation of aliphatic macromolecules in soil humin. *Org. Geochem.* **1996**, *24* (6/7), 651–9.

(63) Lichtfouse, E.; Bardoux, G.; Mariotti, A.; Balesdent, J.; Ballentine, D. C.; Macko, S. A. Molecular ^{13}C and ^{14}C evidence for the allochthonous and ancient origin of C_{16} -C_{18} *n*-alkanes in modern soils. *Geochim. Cosmochim. Acta* **1997**, *9*, 1891–1898.

(64) Lichtfouse, E.; Chenu, C.; Baudin, F.; Leblond, C.; Silva, M. D.; Behar, F.; Derenne, S.; Largeau, C.; Wehrung, P.; Albrecht, P. A novel pathway of soil organic matter formation by selective preservation of resistance straight-chain biopolymers: Chemical and isotope evidence. *Org. Geochem.* **1998**, *28*, 411–415.

(65) Nierop, K. G. J. Origin of aliphatic compounds in a forest soil. *Org. Geochem.* **1998**, *29*, 1009–1016.

(66) Kögel-Knabner, I. The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter. *Soil Biol. Biochem.* **2002**, *34*, 139–162.

(67) Kögel-Knabner, I.; Hatcher, P. G.; Tegelaar, E. W.; De Leeuw, J. W. Aliphatic components of forest soil organic matter as determined by solid-state ^{13}C NMR and analytical pyrolysis. *Sci. Total Environ.* **1992**, *113*, 89–106.

(68) Nguyen, R. T.; Harvey, H. R. Preservation via macromolecular associations during *Botryococcus braunii* decay: Proteins in the Pula Kerogen. *Org. Geochem.* **2003**, *34* (10), 1391–1403.

(69) Simpson, A. J.; Zang, X.; Kramer, R.; Hatcher, P. G. New insights on the structure of algaenan from *Botryoccocus braunii* race A and its hexane insoluble botryals based on multidimensional NMR spectroscopy and electrospray-mass spectrometry techniques. *Phytochemistry* **2003**, *62* (5), 783–796.

(70) Preston, C. M. Applications of NMR to soil organic matter analysis: History and prospects. *Soil Sci.* **1996**, *161* (3), 144–166.

(71) Preston, C. M. Carbon-13 solid-state NMR of soil organic matter using the technique effectively. *Can. J. Soil Sci.* **2001**, *81*, 255–270.

(72) Dria, K. J.; Sachleben, J. R.; Hatcher, P. G. Solid-state carbon-13 nuclear magnetic resonance of humic acids at high magnetic field strengths. *J. Environ. Qual.* **2002**, *31*, 393–401.

(73) Cook, R. L.; Langford, C. H. Structural characterization of a fulvic acid and a aumic acid using solid-state ramp-CP-MAS ^{13}C nuclear magnetic resonance. *Environ. Sci. Technol.* **1998**, *32* (5), 719–725.

(74) Chefetz, B.; Salloum, M. J.; Deshmukh, A. P.; Hatcher, P. G. Structural components of humic acids as determined by chemical modifications and ^{13}C NMR, pyrolysis- and thermochemolysis-GC/MS. *Soil Sci. Soc. Am. J.* **2002**, *66*, 1159–1172.

(75) Simpson, M. J.; Chefetz, B.; Deshmukh, A. P.; Hatcher, P. G. Comparison of polycyclic aromatic hydrocarbon distributions and sedimentary organic matter characteristics in contaminated, coastal sediments from Pensacola Bay, Florida. *Marine Environ. Res.* **2005**, *59* (2), 139–163.

(76) Oren, A.; Chefetz, B. Sorption-desorption behavior of polycyclic aromatic hydrocarbons in upstream and downstream river sediments. *Chemosphere* **2005**, *61* (1), 19–29.

(77) Cuypers, C.; Grotenhuis, T.; Nierop, K. G. J.; Franco, E. M.; de Jager, A.; Rulkens, W. Amorphous and condensed organic matter domains: the effect of persulfate oxidation on the composition of soil/sediment organic matter. *Chemosphere* **2002**, *48* (9), 919–931.

(78) Boyd, S. A.; Xiangcan, J.; Lee, J. F. Sorption of nonionic organic compounds by corn residues from a no-tillage field. *J. Environ. Qual.* **1990**, *19* (4), 734–738.

(79) Kopinke, F. D.; Georgi, A.; Mackenzie, K. Sorption of pyrene to dissolved humic substances and related model polymers. 1. Structure property correlation. *Environ. Sci. Technol.* **2001**, *35*, 2536–2542.

(80) Mashayekhi, H.; Veneman, P.; Xing, B. Phenanthrene sorption by compost humic acids. *Biol. Fertil. Soils* **2006**, *42* (5), 426–431.

(81) Ran, Y.; Sun, K.; Yang, Y.; Xing, B.; Zeng, E. Strong sorption of phenanthrene by condensed organic matter in soils and sediments. *Environ. Sci. Technol.* **2007**, *41* (11), 3952–3958.

(82) Sachleben, J. R.; Chefetz, B.; Deshmukh, A.; Hatcher, P. G. Solid-state NMR characterization of pyrene-cuticular matter interactions. *Environ. Sci. Technol.* **2004**, *38* (16), 4369–4376.

(83) Mao, J. D.; Hundal, L. S.; Thompson, M. L.; Schmidt-Rohr, K. Correlation of poly(methylene)-rich amorphous aliphatic domains in humic substances with sorption of a nonpolar organic contaminant, phenanthrene. *Environ. Sci. Technol.* **2002**, *36* (5), 929–936.

(84) Mao, J. D.; Ding, G. W.; Xing, B. Domain mobility of humic acids investigated with one- and two-dimensional nuclear magnetic resonance: support for dual-mode sorption model. *Commun. Soil Sci. Plant Anal.* **2002**, *33* (9/10), 1679–1688.

(85) Salloum, M. J.; Chefetz, B.; Hatcher, P. G. Phenanthrene sorption by aliphatic-rich natural organic matter. *Environ. Sci. Technol.* **2002**, *36*, 1953–1958.

(86) Shechter, M.; Chefetz, B. Insights into the sorption properties of cutin and cutan biopolymers. *Environ. Sci. Technol.* **2008**, *42* (4), 1165–1171.

(87) Shechter, M.; Xing, B.; Kopinke, F. D.; Chefetz, B. Competitive sorption-desorption behavior of triazine herbicides with plant cuticular fractions. *J. Agric. Food Chem.* **2006**, *54* (20), 7761–7768.

(88) Chen, B.; Johnson, E. J.; Chefetz, B.; Zhu, L.; Xing, B. Sorption of polar and nonpolar aromatic organic contaminants by plant cuticular materials: Role of polarity and accessibility. *Environ. Sci. Technol.* **2005**, *39* (16), 6138–6146.

(89) Chen, B.; Xing, B. S. Sorption and conformational characteristics of reconstituted plant cuticular waxes on montmorillonite. *Environ. Sci. Technol.* **2005**, *39* (21), 8315–8323.

(90) Kang, S. H.; Xing, B. Phenanthrene sorption to sequentially extracted soil humic acids and humins. *Environ. Sci. Technol.* **2005**, *39* (1), 134–140.

(91) Simpson, M. J.; Chefetz, B.; Hatcher, P. G. Phenanthrene sorption to structurally modified humic acids. *J. Environ. Qual.* **2003**, *32* (5), 1750–1758.

(92) Weber, W. J.; Tang, J.; Huang, Q. Development of engineered natural organic sorbents for environmental applications. 1. Materials, approaches, and characterizations. *Environ. Sci. Technol.* **2006**, *40* (5), 1650–1656.

(93) Wang, X.; Xing, B. Sorption of organic contaminants by biopolymer-derived chars. *Environ. Sci. Technol.* **2007**, *41* (24), 8342–8348.

(94) Wang, X.; Xing, B. Importance of structural makeup of biopolymers for organic contaminant sorption. *Environ. Sci. Technol.* **2007**, *41* (10), 3559–3565.

(95) Chen, D.; Xing, B. S.; Xie, W. Sorption of phenanthrene, naphthalene and *o*-xylene by soil organic matter fractions. *Geoderma* **2007**, *139* (3/4), 329–335.

(96) Huang, L.; Boving, T. B.; Xing, B. Sorption of PAHs by aspen wood fibers as affected by chemical alterations. *Environ. Sci. Technol.* **2006**, *40* (10), 3279–3284.

(97) Liang, C.; Dang, Z.; Xiao, B.; Huang, W.; Liu, C. Equilibrium sorption of phenanthrene by soil humic acids. *Chemosphere* **2006**, *63* (11), 1961–1968.

(98) Pan, B.; Ghosh, S.; Xing, B. Nonideal binding between dissolved humic acids and polyaromatic hydrocarbons. *Environ. Sci. Technol.* **2007**, *41* (18), 6472–6478.

(99) Pan, B.; Xing, B.; Liu, W.; Xing, G.; Tao, S. Investigating interactions of phenanthrene with dissolved organic matter: Limitations of Stern−Volmer plot. *Chemosphere* **2007**, *69* (10), 1555–1562.

(100) Wen, B.; Zhang, J. J.; Zhang, S. Z.; Shan, X. Q.; Khan, S. U.; Xing, B. Phenanthrene sorption to soil humic acid and different humin fractions. *Environ. Sci. Technol.* **2007**, *41* (9), 3165–3171.

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