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Sorption Mechanisms of Phenanthrene, Lindane, and Atrazine with Various Humic Acid Fractions from a Single Soil Sample

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 Supporting Information

ABSTRACT: The sorption behavior of organic compounds (phenanthrene, lindane, and atrazine) to sequentially extracted humic acids and humin from a peat soil was examined. The elemental composition, XPS and ¹³C NMR data of sorbents combined with sorption isotherm data of the tested compounds show that nonspecific interactions govern sorption of phenanthrene and lindane by humic substances. Their sorption is dependent on surface and bulk alkyl carbon contents of the sorbents, rather than aromatic carbon. Sorption of atrazine by these sorbents, however, is regulated by polar interactions (e.g., hydrogen bonding). Carboxylic and phenolic moieties are key components for H-bonding formation. Thermal analysis reveals that sorption of apolar (i.e., phenanthrene and lindane) and polar (i.e., atrazine) compounds by humic substances exhibit dissimilar relationships with condensation and thermal stability of sorption domains, emphasizing the major influence of domain spatial arrangement on sorption of organic compounds with distinct polarity. Results of pH-dependent sorption indicate that reduction in sorption of atrazine by the tested sorbents is more evident than phenanthrene with increasing pH, supporting the dependence of organic compound sorption on its polarity and structure. This study highlights the different interaction mechanisms of apolar and polar organic compounds with humic substances.

INTRODUCTION

Soil organic matter (SOM) has been identified as a key sorption medium for organic compounds in soils unless its mass fraction is too low.¹ Because sorption is a critical process affecting environmental behaviors of organic compounds, extensive work has been done to examine the interaction mechanisms between organic compounds and humic substances (HS), which are a type of SOM. Divergent findings on sorption mechanisms have been reported. The different findings could in part result from the HSs originating from diverse precursors and sources. The organic matter in HS from different sources may have different elemental compositions, functionalities, and conformations depending on origin, age, and other environmental factors.^{2,3} Previous studies have shown that these properties of HSs greatly influenced their sorption of organic compounds.^{4–6} To better understand the sorption mechanisms of organic compounds to HSs, humic acids (HAs), and humin (HM) isolated from a single peat soil are studied in this work. The advantage of using HSs from a same source material is to minimize the effect of various minerals, precursors of HSs, and other factors on sorption. However, considering the variability in sorption properties of HSs, studies of the sorption of organic compounds to HSs from a wide range of soils are helpful for a comprehensive understanding of their interactions.²

It has been shown that chemical composition of humic substances and the physical makeup of domains influence organic compound sorption.^{6–8} Much work has been done to probe the roles of various functionalities in HSs, but the debate on the importance of aromatic and aliphatic carbon components

of HS in organic compound sorption is still ongoing. For instance, some works reported the importance of aromatic carbons of geosorbents for organic compound sorption,^{4,9} whereas other studies emphasized the critical roles of aliphatic carbons.^{10,11} It was proposed that H-bonding, hydrophobic interaction, as well as charge transfer mechanisms could be involved in sorption of heterocyclic pseudoaromatic compounds (e.g., atrazine) by HS.^{12–14} However, a consensus on their underlying interaction mechanisms is still not established and the structural features of HS governing sorption of organic compounds remain largely unclear.¹⁵ Till now, a large number of organic compounds of different classes have been used to examine their sorption mechanisms by HS,^{2,16,17} but the influence of chemical structure of HS from a same source material on sorption of organic compounds has rarely been investigated.

It was proposed that organic matter in HSs possesses rubbery and glassy domains,¹⁸ and most previous studies concluded that amorphous domains had higher sorption for organic compounds relative to the condensed ones. For instance, it was reported that organic compounds were sorbed to the expanded mobile amorphous polyethylene domains,¹⁹ which was responsible for their high sorption by plant cuticles^{11,20} and aliphatic-rich HSs.¹⁹ Different from HSs, the carbonaceous materials such as kerogen, coal, and black carbon, as condensed components of organic matter in soils, were reported to dominate organic compound

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sorption over humic acids (HAs), due to their very hydrophobic nature and porous structure.^{21–23} Thus far, little information is available for the relationship between physical makeup of domains and their spatial arrangement in HSs from a same source material and their sorption of organic compounds with distinct composition and structure.

We hypothesize that apolar polycyclic aromatic and polar heterocyclic pseudoaromatic compounds as well as aliphatic compounds would have dissimilar sorption mechanisms by HSs due to their polarity and structural difference. Further, we hypothesize that the effect of physical makeup and spatial arrangement of sorption domains in HSs on organic compound sorption is dependent on the polarity and composition of chemicals. In this study, we also investigate the impact of pH changes on organic compound sorption by HSs in order to unveil their interaction mechanisms. To achieve our research aim, phenanthrene, lindane, and atrazine were selected as sorbates due to their polarity, composition, electron polarizability, and aromaticity differences.

MATERIALS AND METHODS

Humic Substance Fractionation and Sorbates. A peat soil was collected from Amherst, Massachusetts. It was progressively extracted seven times with 0.1 M Na₄P₂O₇ and six times with 0.1 M NaOH and the sequential humic acid fractions obtained were separated from each other. The soil residue after HA extraction was collected as humin. The HA and HM extraction along with their purification and homogenization methods are described elsewhere.⁸ There was no difference in chemical composition between the first and second HA fractions, and between the 12th and 13th HA fractions during the sequential extraction from the peat soil, thus they were respectively combined and labeled as HA1 and HA12. However, there were major structural and compositional differences between HA1 and HA12. The eighth HA fraction was labeled as HA8. The ¹⁴C-labeled and nonlabeled phenanthrene, lindane, and atrazine were purchased from Sigma-Aldrich Chemical Co. and used as sorbates. Selected properties of these chemicals are summarized in Table S1 (Supporting Information (SI)).

Sorbent Characterization. Carbon, hydrogen, and nitrogen contents of HAs and HM were determined using a Vario EL CHN Elemental Analyzer (Germany). Ash contents of all samples were measured by heating at 900 °C for 4 h, and their O contents were calculated by mass difference. Surface elemental composition and carbon-based functionalities of all samples were determined using an AXIS-Ultra X-ray Imaging Photoelectron Spectrometer (Kratos Analytical Ltd. UK) with a monochromatic Al K α radiation source operated at 225 W, 15 mA, and 15 kV. It is noted that there could be a bit of difference between the 3-D conformation of HSs in solid and aqueous environment. The solid-state cross-polarization magic angle-spinning and total-sideband-suppression ¹³C NMR spectra of all samples were obtained with a Bruker Avance III 400 MHz NMR Spectrometer (Bruker Corporation, Germany) operated at ¹³C frequency of 100 MHz to get their structural information. The NMR running parameters and chemical shift assignments are presented in the SI.

Zeta Potential Measurements. Zeta potential of HAs and HM at different pH values was measured with a ZetaSizer Nano Series Instrument (Malvern Instrument Ltd.) in duplicate and the averaged data are presented for discussion. Sodium chloride

solution (0.01 M) was used as background electrolyte and 0.01 M HCl was used to adjust pH of samples.²⁴ A concentration of 60 mg/L was used for both HAs and HM.

Thermal Gravimetric and Differential Scanning Calorimetric Analysis. For TGA analysis, around 5 mg of dry HA and HM sample was scanned with a Thermogravimetric Analyzer (TGA Q50, TA Instruments) from 25 to 945 °C at a heating rate of 10 °C/min. Before TGA analysis, all samples were freeze-dried and stored in a desiccator. The glass transition temperature (*T_g*) of HAs and HM was determined using a differential scanning calorimeter (DSC 2010, TA Instruments). DSC analysis was performed with a heating rate of 5 °C/min and N₂ as a purge gas. Approximately 5 mg of dry HAs or HM and hermetically sealed standard aluminum pans were used for DSC experiments. To keep the samples dry, all HSs were treated in the identical approach as for TGA analysis.

Organic Compound Sorption Experiment. Sorption isotherms of phenanthrene, lindane and atrazine by HAs and HM were obtained using a batch equilibration technique in screw cap vials with aluminum foil-Teflon liners. Stock solutions of ¹⁴C labeled phenanthrene, lindane, and atrazine as well as nonlabeled phenanthrene and lindane were prepared by dissolving them in methanol, while that of nonlabeled atrazine was made in water. Test solutions were prepared by adding ¹⁴C labeled and non-labeled stock solutions of the tested compounds to the background solution containing 0.01 M CaCl₂ to maintain a constant ionic strength and 100 mg/L of NaN₃ to minimize biodegradation. After shaking for 1 h, they were slowly added to vials containing an appropriate amount of HS, ensuring that as little headspace as possible remained. The sample mass added to each of the vials was selected to obtain 20–80% uptake of sorbate at equilibrium. The methanol concentration in aqueous phase was always below 0.1% (v/v) to minimize the cosolvent effect. All vials were sealed with aluminum foil-lined Teflon screw caps and placed on a rotary shaker to mix for 9 days at room temperature (23 ± 1 °C). Our preliminary test indicated that equilibrium was reached within 8 days. All vials were centrifuged at 3000 rpm for 30 min after mixing, and then 2 mL of supernatant was sampled and added to scintiverse cocktail (4 mL) (Fisher Scientific Co.) for scintillation counting. All samples, including blanks, were run in duplicate. Due to negligible mass loss of sorbates as indicated in the blanks (<3%), their uptake by all samples was calculated by mass difference.

pH-Dependent Sorption. To examine the influence of pH change, sorption tests of phenanthrene and atrazine at various pH points were performed. Before phenanthrene and atrazine addition, the pH of HA and HM suspensions was adjusted with 0.1 M HCl or 0.1 M NaOH. An intermediate concentration of phenanthrene (0.5 mg/L) and atrazine (13 mg/L) was used. The various pH level samples along with blanks were run in duplicate. The averaged sorption data of phenanthrene and atrazine are presented for discussion. All other experimental parameters including solid-to-solution ratios, mixing time, and centrifugation were identical to those for the sorption experiments.

Sorption Isotherm Model. Sorption data of phenanthrene, lindane and atrazine by HAs and HM were fitted with the logarithmic form of Freundlich model:

$$\log Q = \log K_f + n \log C_e$$

where *Q* and *C_e* are solid (mg/kg)- and liquid-phase (mg/L)

Table 1. Bulk Elemental Composition and Atomic Ratios, Surface Functionalities and Elemental Composition and Integrated Solid-State ^{13}C NMR Data of Humic Acids and Humin^a

samples	integrated results of solid-state ¹³ C NMR spectra									bulk elemental composition						
	distribution of C chemical shift, ppm (%)						aliphatic C	polar C	aliphatic polar C	C (%)	H (%)	O (%)	N (%)	Ash (%)	(O+N)/C	
	0–50	50–109	109–145	145–163	163–190	190–220										
HA1	32	31	19	6	11	1	63	49	31	48.5	4.38	37.8	2.86	6.5	0.63	
HA8	39	32	14	5	8	1	71	46	32	53.5	5.97	35.6	3.18	1.8	0.55	
HA12	49	29	10	3	7	1	78	40	29	58.4	7.04	31.0	2.88	0.7	0.44	
HM	55	27	10	3	4	0	82	34	27	45.6	5.59	25.4	1.46	22.0	0.45	
surface functionalities and elemental composition (%)																
	C—C	C—O	C=O	COO	Na	Fe	O	N	C	S	P	Si	Al	Cl	(O+N)/C	S _{(O+N)/C} /B _{(O+N)/C}
HA1	32.8	10.4	3.3	3.7	4.4	2.3	33.3	1.6	50.1		4.5	0.3		3.5	0.53	0.84
HA8	32.7	16.7	5.9	3.2	2.5	1.0	27.4	4.1	58.6	0.3	2.2	0.5	0.5	2.9	0.41	0.75
HA12	43.0	18.2	6.3	3.9	0.9	0.7	21.6	3.2	71.4	0.1		1.0	0.3	0.9	0.27	0.61
HM	55.6	9.2	5.3	4.7	2.1	0.9	17.7	0.7	74.7			2.6	1.1	0.1	0.19	0.42

^a Aliphatic C (%): total aliphatic C region (0–109 ppm); polar C (%): total polar carbon region (50–109 ppm and 145–220 ppm); aliphatic polar C (%): polar carbon in aliphatic region (50–109 ppm); $S_{(\text{O+N})/\text{C}}/B_{(\text{O+N})/\text{C}}$: ratio of surface to bulk polarity. It is evident that with successive HA isolation, the alkyl and total aliphatic carbon content of HSs increased, but their polar carbon content decreased. The surface and bulk oxygen content, surface polarity as well as the ratio of surface to bulk polarity of HSs decreased with progressive HA extraction.

concentrations of sorbate, respectively. K_f is sorption coefficient ((mg/kg)/(mg/L)ⁿ), and n (dimensionless) is a site energy heterogeneity factor, often used as an indicator of isotherm nonlinearity. The least-squares linear regression method was employed to calculate $\log K_f$ and n values which assumes there is no error in C_e . This may influence the resulting n and $\log K_f$ values.

RESULTS AND DISCUSSION

HA and HM Property Characterization. With progressive HA fractionation, the oxygen and polar carbon contents of HSs gradually decrease from 37.8% and 49% for HA1 to the lowest values of 25.4% and 34% for HM, respectively (Table 1). This suggests that organic matter with a higher abundance of hydrophilic functionalities has higher water solubility relative to the fractions rich in hydrophobic components. Hence, the organic matter with abundant hydrophilic moieties is readily extracted in HA fractionation process, eventually leaving more hydrophobic components tightly bound to minerals in HM.²⁵ Further, the aliphatic carbons were speculated to be more tightly bound to minerals relative to the aromatic ones because abundance of the aromatic components decreased with progressive HA extraction.²⁵ The surface polarity and polar carbon content of HSs are much lower than the corresponding bulk values, indicating that a majority of hydrophilic functionalities are in their interior part, leaving the hydrophobic moieties facing outside. Furthermore, ratio of the surface to bulk polarity of HSs decreases with sequential HA extraction (i.e., from 0.84 to 0.42) (Table 1), implying that their surface polarity decreases more, evidently, than the bulk particles in this process.

Roles of Polarity, Functionalities, and H-bonding in Sorption of Phenanthrene, Lindane and Atrazine by HSs. Sorption isotherms of phenanthrene, lindane, and atrazine by HSs are presented in SI Figure S1, and the sorption data were well fitted

with Freundlich model as indicated by the high R^2 values (all >0.985) (Table 2). It was documented in previous studies that polarity of geosorbents (e.g., HS and black carbons) plays a critical role in sorption of various organic compounds, despite having very different chemical composition and structure.^{5,26} It is hypothesized that geosorbents of higher polarity would have lower sorption for organic compounds, because they have substantial hydrophilic moieties, which can provide sites for water cluster formation at their surfaces through H-bonding. Water clusters reduce the surface hydrophobicity of sorbents and the accessibility of organic compound molecules to sorption domains, as well as compete with sorbate for sorption sites, thus reducing their sorption. Such a mechanism can well explain the negative correlation of sorption of HSs for apolar compounds phenanthrene and lindane with their surface and bulk polarity, but this does not account for the positive correlation relationship for the polar compound atrazine (Figure 1). A possible explanation to account for this dissimilar relationship is that sorption of phenanthrene, lindane and atrazine by HSs follows different mechanisms due to their structure and polarity difference.

With sequential HA extraction, K_{oc} (organic carbon content-normalized sorption coefficient) values of phenanthrene and lindane by HSs respectively increased by 1.59 and 2.88 times, but K_{oc} values of atrazine decreased by 64% (SI Figure S1, Table 2). K_{oc} values of phenanthrene and lindane by HSs were positively correlated with their hydrophobic carbon content (sum of alkyl and aromatic carbon content) ($r^2 = 0.838$, $p < 0.06$ for phenanthrene and $r^2 = 0.241$ for lindane), implying that nonspecific interaction mechanism dominated sorption of phenanthrene and lindane. However, such a mechanism cannot dominate sorption of atrazine since its K_{oc} values are negatively correlated with their hydrophobic carbon content (SI Figure S1, Tables 1 and 2).

K_{oc} values of phenanthrene and lindane by HSs are positively correlated with their surface and bulk alkyl carbon contents

Table 2. Parameters of Freundlich Model-Based Sorption Isotherm Fitting for Phenanthrene, Lindane, and Atrazine by Humic Substances^a

compound	sorbent	K_f	n	R^2	K_{oc} (0.4 S_w)	L/S (mL/mg)
phenanthrene	HA1	3.672 ± 0.017	0.819 ± 0.018	0.991	11100	8/1.5
	HA8	4.005 ± 0.013	0.899 ± 0.013	0.996	20400	8/1
	HA12	4.109 ± 0.018	0.915 ± 0.020	0.994	23500	40/1.8
	HM	4.076 ± 0.025	0.877 ± 0.028	0.985	28700	40/1.8
lindane	HA1	2.658 ± 0.004	0.924 ± 0.009	0.999	865	8/7
	HA8	3.102 ± 0.005	0.939 ± 0.011	0.998	2210	8/3
	HA12	3.312 ± 0.004	0.958 ± 0.010	0.999	3360	8/2
	HM	3.013 ± 0.011	0.929 ± 0.023	0.993	2100	8/4
atrazine	HA1	2.375 ± 0.021	0.916 ± 0.021	0.991	394	8/23
	HA8	2.220 ± 0.011	0.948 ± 0.011	0.998	271	8/26
	HA12	2.235 ± 0.013	0.977 ± 0.013	0.997	277	4/8.5
	HM	1.893 ± 0.023	0.924 ± 0.022	0.991	141	8/48

^a S_w : aqueous solubility (mg/L); K_{oc} : organic carbon content-normalized sorption coefficient (L/kg); L/S : liquid-to-solid ratio (mL/mg).

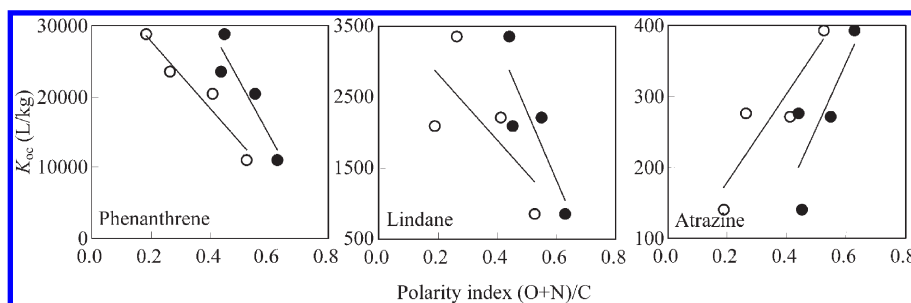


Figure 1. Relationship between K_{oc} (organic carbon content-normalized sorption coefficient) values of phenanthrene, lindane and atrazine by HSs and their surface and bulk polarity. Open circles are for surface polarity and the closed ones are for bulk polarity. $K_{oc, \text{phenanthrene}} = -47800S_{pi} + 37700$, ($r^2 = 0.948$, $p < 0.05$) = $-76100B_{pi} + 60300$, ($r^2 = 0.857$, $p < 0.05$); $K_{oc, \text{lindane}} = -4650S_{pi} + 3760$, ($r^2 = 0.472$) = $-9600B_{pi} + 7100$, ($r^2 = 0.717$) and $K_{oc, \text{atrazine}} = 624S_{pi} + 52$, ($r^2 = 0.827$) = $912B_{pi} - 201$, ($r^2 = 0.630$). Here S_{pi} and B_{pi} are surface and bulk polarity of sorbents.

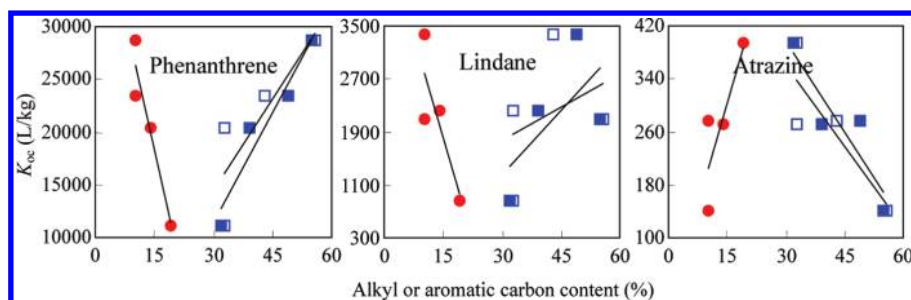


Figure 2. Relationship between K_{oc} values of phenanthrene, lindane and atrazine by humic acids and humin and their surface (blue \square) and bulk (blue \blacksquare) alkyl carbon contents, as well as bulk aromatic carbon contents (red \bullet). $K_{oc, \text{phenanthrene}} = 576S_{\text{alkyl C}} - 2720$, ($r^2 = 0.716$) = $696B_{\text{alkyl C}} - 9510$, ($r^2 = 0.929$, $p < 0.05$) = $-1650B_{\text{aromatic C}} + 42800$, ($r^2 = 0.913$); $K_{oc, \text{lindane}} = 33S_{\text{alkyl C}} + 772$, ($r^2 = 0.125$) = $65B_{\text{alkyl C}} - 730$, ($r^2 = 0.432$) = $-203B_{\text{aromatic C}} + 4820$, ($r^2 = 0.723$); $K_{oc, \text{atrazine}} = -8S_{\text{alkyl C}} + 607$, ($r^2 = 0.740$) = $-9B_{\text{alkyl C}} + 671$, ($r^2 = 0.820$) = $20B_{\text{aromatic C}} + 2$, ($r^2 = 0.702$). K_{oc} values of phenanthrene and lindane by HSs are negatively correlated with their bulk aromatic carbon content, but positively correlated with their surface and bulk alkyl carbon contents. Conversely, K_{oc} values of atrazine by HSs are positively correlated with their bulk aromatic carbon content, but negatively correlated with their surface and bulk alkyl carbon contents. P-test shows that the correlation between K_{oc} values of phenanthrene and bulk alkyl carbon content of HSs is significant. Here, $S_{\text{alkyl C}}$, $B_{\text{alkyl C}}$, and $B_{\text{aromatic C}}$ are surface and bulk alkyl carbon content (%), as well as bulk aromatic carbon content (%), respectively.

(Figure 2). This implies that sorption of phenanthrene and lindane is dependent on their abundance of surface and bulk alkyl carbon domains. On the other hand, sorption of atrazine is negatively correlated with the surface and bulk alkyl carbon

contents of HSs (Figure 2, Tables 1 and 2). This last result contradicts a previous study, which demonstrated that aliphatic carbon content of HAs was one of key factors regulating their sorption for atrazine.¹⁵ The difference between the previous and

the present study could be that the HAs used in the previous study were extracted from a volcanic soil using four distinct methods, and the soil was different from ours. Therefore, the HAs used in two studies had quite different chemical composition and structure.

The K_{oc} values of phenanthrene and lindane by HSs are inversely correlated with their aromatic carbon contents (Figure 2, Tables 1 and 2). A similar relationship between sorption of phenanthrene by tea leaves and nonhydrolyzable components of surface soils and sediments and their aromatic carbon contents was reported elsewhere.^{27,28} Xing⁴ also reported that sorption of naphthalene by HS decreased with an increase in aromatic carbon content. On the other hand, Johnson et al.²⁹ and Tang et al.³⁰ used subcritical superheated water treatment to remove hydrophilic components from soils, pine needles, barks, oak and pine leaves to mimic the influence of diagenesis-like process on composition and structure of HS, for probing the impact of organic matter alteration on phenanthrene sorption. A positive correlation between K_{oc} values of phenanthrene and aromatic carbon content of samples was observed. Taking these studies together, it may be concluded that for fresh organic matter in peat soil alkyl carbon components rather than aromatic ones are predominant hydrophobic domains for sorption of phenanthrene and lindane. In contrast, for mature HS that underwent geological alteration aromaticity played a critical role in their sorption for polycyclic aromatic hydrocarbons. The K_{oc} values of phenanthrene by individual HSs are higher than lindane, due to its stronger van der Waals interactions with the organic matter in these sorbents (SI Figure S1 and Table S1, and Table 2). After K_{oc} values of these two compounds were normalized with their respective K_{ow} values, K_{oc}/K_{ow} values of phenanthrene were still 1.19–2.32 times that of lindane. This could be a result of the contributions of π – π interactions between phenanthrene and aromatic components in HSs, and the much stronger van der Waals interaction between the aliphatic entities in HSs and an aromatic compound than an aliphatic one, assuming they had identical hydrophobicity (e.g., K_{ow}).

It is, in theory, plausible that atrazine is able to interact with HSs through π – π interactions. Our data correspondingly show a positive correlation between aromatic carbon contents of HSs and K_{oc} values of atrazine (Figure 2, Tables 1 and 2), which seemingly supports such a mechanism. Consistent with our observation, it was reported elsewhere that K_{oc} values of atrazine by HAs were positively correlated with their aromatic carbon contents ($r = 0.91$).⁹ However, further analysis on our data reveals that sorption of atrazine to the tested HSs cannot be dominated by such a mechanism. Otherwise, K_{oc} values of phenanthrene by HAs and HM should also have been positively correlated with their aromatic carbon contents, contrary to our observation.

A positive correlation between K_{oc} values of atrazine by HSs and their polar carbon contents indicate that H-bonding between this compound and O-containing moieties in HSs could play an important role in their interactions (SI Figure S2). The lone-pair electrons on the nitrogen atom of atrazine are able to delocalize to the triazine ring, thus creating polarity and a tendency to form H-bonding with O-containing polar functionalities in HS.³¹ Polar moieties on HS facilitate water sorption, and the amino nitrogen atoms of atrazine are able to act as H-bonding acceptors with the strongly adsorbed water molecules.³² Welhouse and Bleam³¹ further reported that H-bonding between atrazine and acid

functionalities of HAs was a key mechanism governing sorption. Our data further show that the abundance of carboxylic and phenolic carbon components of HSs is positively correlated with their sorption for atrazine (SI Figure S3), strongly supporting that these two components of HSs are principal functionalities for H-bonding formation with atrazine. Sullivan et al.³³ also proposed that H-bonding between atrazine and carboxylic and phenolic moieties of HSs from a muck, a silty clay loam and a latosol sandy loam was likely the dominating sorption mechanism. Inconsistently, no correlation between sorption of atrazine by humic materials from three typical Mediterranean soils and their carboxylic carbon content was observed.³⁴ Aside from H-bonding, Kulikova et al.⁹ proposed that van der Waals force could affect sorption of this compound by HSs.

Roles of Thermal Stability of Domains and Their Spatial Arrangement in HSs in Sorption of Phenanthrene, Lindane, and Atrazine. The ^{13}C NMR spectra of all samples have two peaks at 30 and 33 ppm (SI Figure S4), which are characteristics of long polyethylene chain structures. These two peaks can be assigned to amorphous and crystalline alkyl carbon domains, respectively.⁶ The peak at 33 ppm tends to be sharper relative to that at 30 ppm with progressive HA extraction, demonstrating the increasingly compacted structure of organic matter in HAs and HM. Consistently, our TGA data indicate that the decomposition temperature of HSs increases with HA isolation (with values of 209.8 °C for HA1, 225.4 °C for HA8, 237.9 °C for HA12 until 452.2 °C for HM), suggesting the elevated thermal stability of sorption domains. The high decomposition temperature of HM suggests that it could contain some recalcitrant black carbon. However, high thermal stability of organic matter in HM could also be due to its strong interactions with minerals. No T_g values were detected for HAs, but humin gave a T_g value of 79.75 °C. Conversely, it was reported that a Suwannee River fulvic acid and a peat soil humic acid had T_g values in 36–49 °C and 43–62 °C, respectively.^{7,35} The difference in physical makeup of HAs and HM could result from HAs having heterogeneous chemical composition and thus domains of varying mobility, whereas HM has relatively more homogeneous composition and well developed glassy domains. Due to strong interactions of organic matter with minerals in HM, highly condensed domains were developed at their interfaces. The compacted domains in HAs were likely created by rearrangement and entanglement of long polyethylene chains in the recrystallization process during their isolation. It was difficult for macromolecules in HAs to create well-arranged and highly compacted structures,¹⁸ because reconstitution of HAs was achieved by rapid precipitation in acidic conditions (i.e., pH \approx 1.5). Such a trend could be more pronounced for the first isolated fractions.

K_{oc} values of phenanthrene and lindane by HSs increased with increasing thermal stability and condensation of sorption domains, whereas these values for atrazine decreased ($p < 0.05$) (SI Figures S1 and S4, Table 2). Different relationships between condensation of domains in HSs and their sorption for phenanthrene, lindane, and atrazine highlights the influence of domain spatial arrangement on sorption of organic compounds with distinct polarity. Since the abundance of hydrophobic domains at the external surfaces of HAs and HM is much higher than their interior parts and nonspecific interactions dominate sorption of phenanthrene and lindane to these domains as stated above (Figure 1, Table 1), these domains are accessible to these two compounds and such a domain spatial arrangement facilitates their sorption. With development of thermal stability and

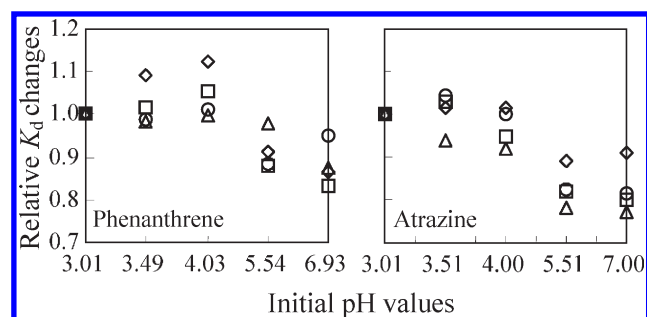


Figure 3. Effect of solution pH on sorption of phenanthrene and atrazine by HSs. HA1 (\diamond); HA8 (\square); HA12 (Δ); HM (\circ). The y axis represents the ratio of K_d values of phenanthrene and atrazine by humic substances at various pH points to that at pH 3.01.

condensation of polyethylene domains in HSs, there would be an increasing number of high-energy sites in microvoids which may enhance phenanthrene and lindane sorption. The condensed and crystalline domains at the external surfaces of HA and HM particles reduce accessibility of atrazine molecules to O-containing polar functionalities in their interior part, which are responsible for sorption of this compound (SI Figure S5). Therefore, an increase in abundance of condensed and crystalline domains at the HS particle surfaces more strongly reduce their sorption for atrazine.

Sorption of the tested compounds by HAs is slightly nonlinear, due partly to the heterogeneous composition and compacted domains. The isotherm tends to be more linear with HA isolation because the composition of organic matter in HAs becomes more homogeneous as extraction proceeds. Humic exhibits slightly more nonlinear sorption for the tested compounds than HA12 (Table 2). This could be due to the added presence of minerals compared to HA, as a greater diversity of sorption sites can be created along organic matter-mineral interfaces than simply organic matter on its own.

Effect of pH Changes on Sorption of Phenanthrene and Atrazine by HAs and HM. To gain further insight into the sorption mechanisms of apolar and polar aromatics by HSs, the influence of pH changes on sorption of phenanthrene and atrazine by HAs and HM was examined. Our data show that zeta potential of HSs decreases with increasing pH (SI Figure S6). The influence of pH on sorption of atrazine by HSs is 3.2–10.2% greater than phenanthrene at pH 5.5–7 (Figure 3). HSs have high sorption for both phenanthrene and atrazine at $\text{pH} \leq 4$, but the sorption decreases with increasing pH (Figure 3). A previous study reported that the maximum adsorption of atrazine by sediments appeared at pH close to its pK_a (1.7), where half of atrazine is present in cationic form and the other half is in molecular form.³⁶

As a weak-base, atrazine would be protonated at low pH values, and this protonation favors increased sorption by HSs via ionic interactions.³⁷ The acidic functionalities at HA and HM surfaces tends to be less negatively charged as pH decreases until they are protonated when pH drops to approximately 3.5, thus giving a positive zeta potential value (SI Figure S6). As pH increases, a greater portion of acidic functionalities in HSs dissociate and ionize as indicated by the increased negative zeta potentials, thereby making their surfaces more negatively charged and decreasing the H-bonding with atrazine (SI Figure S6). Atrazine is negligibly protonated at $\text{pH} > 4$,³⁶ thus ionic interactions with HAs and HM are negligible. In addition, the

organic matter in HAs and HM has a higher abundance of hydrophobic sites at lower pH values than at higher ones (e.g., pH below vs above the point of zero charge of sorbent),¹² so they have stronger nonspecific interactions with atrazine at lower pH points. Therefore, sorption of atrazine by HSs decreases with increasing pH values.

As an apolar compound, phenanthrene is unable to be sorbed to HAs and HM through ionic interactions at both lower and higher pH values. The only point is that the organic matter in HAs and HM may have higher nonspecific interactions with phenanthrene at lower relative to higher pH values, due to its more hydrophobic nature. Hence, reduction in sorption of phenanthrene by HSs resulting from pH increase is less marked than for atrazine.

■ ASSOCIATED CONTENT

S Supporting Information. Selected physicochemical properties of the chemicals used (Table S1); Organic carbon content-normalized sorption isotherms (Figure S1); Relationship between K_{oc} values of atrazine by HSs and their polar carbon contents (Figure S2); Relationship between K_{oc} values of atrazine by HSs and their carboxylic and phenolic carbon contents (Figure S3); Solid-state ^{13}C NMR spectra of HSs (Figure S4); Schematic diagram of HA and HM structure and the difference in sorption mechanisms of phenanthrene, lindane and atrazine by HSs (Figure S5); Zeta potential of HSs as a function of pH (Figure S6). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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